



AGRICULTURAL RESEARCH INSTITUTE
PUSA

THE JOURNAL
OF THE
American Chemical Society

VOL. XXXVII

JANUARY—JUNE
1915

Editor:

WILLIAM A. NOYES.

Associate Editors:

**M. T. BOGERT,
C. A. BROWNE,
EDWARD HART,
W. F. HILLEBRAND,
JOHN JOHNSTON,**

**J. H. LONG,
W. LASH MILLER,
CHARLES L. PARSONS,
JULIUS STIEGLITZ,
H. W. WILEY.**

**EASTON, PA.:
ESCHENBACH PRINTING COMPANY
1915**

Papers.

January.

General, Physical and Inorganic.

| | |
|---|-----|
| Ira Remsen: The Development of Chemical Research in America..... | 1 |
| T. W. Richards and F. O. Anderegg: The Inclusion of Electrolyte by the Deposit in the Silver Voltameter..... | 7 |
| Hugh Stott Taylor: The Interaction of Hydrogen and Chlorine under the Influence of Alpha Particles..... | 24 |
| Alexander Smith and Robert H. Lombard: The Densities and Degrees of Dissociation of the Saturated Vapors of the Ammonium Halides, and the Related Thermal Data..... | 38 |
| G. A. Linhart: On the Rate of Reduction of Mercuric Chloride by Sodium Formate..... | 70 |
| George McPhail Smith: The Effect upon their Solution Tensions of Dissolving the Alkali and Alkali Earth Metals in Mercury, and the Constitution of such Solutions..... | 76 |
| Theodore W. Richards and Thorbergur Thorvaldson: A New Thermochemical Method for Subdividing Accurately a Given Interval on the Thermometer Scale..... | 81 |
| Edward Ellsworth Marbaker: The Separation of Tungsten from Molybdenum.. | 86 |
| Theodore W. Richards and Charles R. Hoover: The Molecular Weight of Sodium Sulfate and the Atomic Weight of Carbon Referred to Silver and Bromine... | 95 |
| Theodore William Richards and Charles R. Hoover: The Molecular Weight of Sodium Sulfate and the Atomic Weight of Sulfur..... | 108 |
| Gregory Paul Baxter and Miner Louis Hartmann: A Revision of the Atomic Weight of Cadmium..... | 113 |
| L. M. Dennis and B. J. Lemon: The Electrolysis of Solutions of the Rare Earths. | 131 |
| Merle Randall and F. Russell v. Bichowsky: Vacuum and Pressure Stopcocks... | 137 |
| Notes: Blast-Lamp for Natural Gas; A Modified Kipp Generator; An Improved Heating Apparatus for Maintaining Constant Temperature in Work with Polarimeters and Refractometers; Measurement of the Vapor Pressures of Solutions..... | 144 |

Organic and Biological.

| | |
|--|-----|
| James Kendall and Willis A. Gibbons: The Addition Compounds of Aldehydes and Ketones with Organic Acids..... | 149 |
| Treat B. Johnson and Edward F. Kohmann: 3-Nitro-4-hydroxycinnamic Acid and its Methyl Ether..... | 162 |
| Alfred E. Sherndal: On the Blue Hydrocarbon Occurring in Some Essential Oils. | 167 |
| Treat B. Johnson and Sidney E. Hadley: Researches on Hydantoins. XXIX. Geometrical Isomerism in the Hydantoin Series..... | 171 |
| Treat B. Johnson and Howard F. Haggard: Researches on Pyrimidines. LXXIII. Alkylation of 2-Mercaptopyrimidines..... | 177 |
| E. W. Esslinger and S. F. Acree: On 1-Phenyl-4,5-dihydro-5-oxy-3-triazolylsulfonic Acid and 1-Phenyl-4,5-dihydro-5-oxy-3-triazolylmethylsulfone..... | 183 |
| William A. Noyes and Ralph S. Potter: The Valence of Nitrogen in Ammonium Salts..... | 189 |
| T. B. Aldrich: On the Presence of Histidine-like Substances in the Pituitary Gland (Posterior Lobe)..... | 203 |

| | |
|--|-----|
| Robert A. Hall: Tri-ammonium Citrate..... | 208 |
| K. George Falk and K. Sugiura: Studies on Enzyme Action. XII. The Esterase and Lipase of Castor Beans..... | 217 |
| Thos. G. Thompson: The Total Amino Nitrogen in the Seedlings of the Alaska Pea..... | 230 |
| New Books: Landolt-Börnstein Physikalisch-Chemische Tabellen; Notes on Elementary Inorganic Chemistry; Manual of Quantitative Chemical Analysis; Principles of Quantitative Analysis. An Introductory Course; Monographs on Inorganic and Physical Chemistry; Outlines of Organic Chemistry; A Study of Foods..... | 236 |

February.

General, Physical and Inorganic.

| | |
|---|-----|
| Grinnell Jones and Miner Louis Hartmann: A Study of the System: Water, Potassium Iodide and Iodine at Zero Degrees..... | 241 |
| G. A. Linhart: On the Association of Mercuric Chloride in Water Solution..... | 258 |
| J. M. Nelson and K. George Falk: The Electron Conception of Valence. VI. Inorganic Compounds..... | 274 |
| Gregory Paul Baxter: A Search for an Alkali Element of Higher Atomic Weight than Cesium..... | 286 |
| H. W. Foote: A Method of Determining the Hydrates Formed by a Salt..... | 288 |
| Jnanendranath Mukhopadhyaya: Electric Synthesis of Colloids..... | 292 |
| Louis J. Curtman and Alan G. Wikoff: The Detection of Bromides in the Presence of Thiocyanates, Cyanides and Ferrocyanides..... | 298 |
| M. A. Rosanoff and C. W. Bacon: On Fractional Distillation with Regulated Stillheads..... | 301 |
| Edward W. Washburn and Edward O. Heuse: The Measurement of Vapor Pressure Lowering by the Air Saturation Method..... | 309 |
| Note: Nitrochrome Gauze..... | 321 |

Organic and Biological.

| | |
|---|-----|
| Richard Willstätter: Chlorophyll..... | 323 |
| Oscar F. Hedenburg: On the Esters, as Well as the Monomolecular β - and γ -Lactones, of <i>d</i> -Mannonic and <i>d</i> -Gluconic Acids; on Ortho-Bis- <i>d</i> -Galactonic Acid, <i>d</i> -Galactonic γ -Lactone and Its Mono-hydrate..... | 345 |
| Lambert Thorp and E. A. Wildman: Syntheses in the Diphenylmethane Series..... | 372 |
| Treat B. Johnson and E. Heaton Hemingway: Researches on Pyrimidines. LXXIV. Synthesis of 4-Phenylcytosine..... | 378 |
| Treat B. Johnson and Joseph S. Bates: Researches on Hydantoins. XXX. Stereoisomeric Modifications of Benzalhydantoin..... | 383 |
| G. B. Frankforter and W. Kritchevsky: The Action of Chloral, Bromal and Benzaldehyde on the Polycyclic Hydrocarbons in the Presence of Aluminium Chloride..... | 385 |
| George A. Burrell and Frank M. Seibert: The Separation of the Constituents in a Natural Gas from which Gasoline is Condensed..... | 392 |
| E. Newton Harvey: Experiments on the Nature of the Photogenic Substance in the Firefly..... | 396 |
| F. Alex. McDermott: Experiments on the Nature of the Photogenic Processes in the Lampyridae..... | 401 |
| New Books: Qualitative Chemical Analysis; Food Products; Methods of Quantitative Organic Analysis..... | 404 |

March.**General, Physical and Inorganic.**

| | |
|---|-----|
| Gregory Paul Baxter: Twenty-Second Annual Report of Committee on Atomic Weights. Determinations Published during 1914..... | 407 |
| Irving Langmuir: The Dissociation of Hydrogen into Atoms. Part II. Calculation of the Degree of Dissociation and the Heat of Formation..... | 417 |
| Gilbert N. Lewis and Merle Randall: The Free Energy of Some Carbon Compounds..... | 458 |
| Theodore W. Richards and Edward P. Bartlett: Compressibilities of Mercury, Copper, Lead, Molybdenum, Tantalum, Tungsten and Silver Bromide..... | 470 |
| Leason H. Adams: The Measurement of the Freezing-Point Depression of Dilute Solutions..... | 481 |
| T. W. B. Welsh: Anhydrous Hydrazine. II. Electrolysis of a Solution of Sodium Hydrazide in Anhydrous Hydrazine..... | 497 |
| A. Thiel: The Solubility of Certain Difficultly Soluble Silver Salts..... | 508 |
| Arthur E. Hill: The Relative Solubility of Certain Silver Salts..... | 510 |
| Marks Neidle: Absorption and the Surface Tensions of Aqueous Solution of Homologous Fatty Acids and Alcohols..... | 513 |
| Gregory Paul Baxter and Olus Jesse Stewart: A Revision of the Atomic Weight of Praseodymium. The Analysis of Praseodymium Chloride..... | 516 |
| Jas. Lewis Howe: Recent Work in Inorganic Chemistry..... | 536 |
| Note: A Surficial Burn Produced by an Unknown Radiation..... | 549 |

Organic and Biological.

| | |
|---|-----|
| Hugh Stott Taylor: The Influence of Temperature in Acid Catalysis..... | 551 |
| H. N. K. Rørdam: Organic Oxonium Compounds. I. Dimethylpyronehydrochloride..... | 557 |
| Rasik Lal Datta and Nihar Ranjan Chatterjee: The Production of Chloropicrin by the Action of Aqua Regia on Organic Compounds..... | 567 |
| Rasik Lal Datta and Satyaranjan Das Gupta: Contributions to the Knowledge of Halogenation. VII. Substituted Nitrogen Chlorides. The Action of Chlorine on Carbamic Esters and Biurets and the Preparation of Chlorocarbamic Esters and Chlorobiurets..... | 569 |
| Rasik Lal Datta and Satyaranjan Das Gupta: Contributions to the Knowledge of Halogenation. VIII. New Series of Chlorohydroxy Compounds. The Hydrolytic Chlorination of Dimethylpyrone. The Isolation of 2,6-Dichlorohydroxy-3,5-Dichloro-4-Ketoheptane and Its Decomposition into 3,5-Dichloro-2,4,6-Trioxiheptane..... | 578 |
| John B. Ekeley and Charles F. Poe: The Action of Acetic Anhydride on Some Benzylidene Anthranilic Acids. IV..... | 582 |
| D. Breese Jones: The Action of Finely Divided Silver on α -Bromo- and α -Iodopalmic Acids; Synthesis of Two Isomeric Ditetradecylsuccinic Acids..... | 586 |
| William J. Hale and Arthur G. Williams: The Constitution of Acetylacetone-Thiourea..... | 594 |
| Arno Viehoveer and Carl O. Johns: On the Determination of Small Quantities of Hydrocyanic Acid..... | 601 |
| Harry W. Redfield and Clarence Huckle: A Comparative Study of Methods for the Quantitative Determination of Sulfur in Peptide..... | 607 |
| Harry W. Redfield and Clarence Huckle: Quantitative Determinations of Sulfur in the Culture Medium for the Detection of the Bacteria Producing Hydrogen Sulfide..... | 612 |

| | |
|--|-----|
| H. C. Sherman and A. W. Thomas: Studies on Amylases. VIII. The Influence of Certain Acids and Salts upon the Activity of Malt Amylase..... | 623 |
| H. C. Sherman and M. D. Schlesinger: Studies on Amylases. IX. Further Experiments upon the Purification of Malt Amylase..... | 643 |
| K. George Falk: Studies on Enzyme Action. XIII. The Lipase of Soy Beans.. | 649 |
| H. M. English and C. G. MacArthur: Enzymes of the Central Nervous System. | 653 |
| Note: The Origin of Petroleum..... | 664 |
| New Books: Essays and Addresses; Zur Lehre von den Zuständen der Materie; Handbuch der Arbeitsmethoden in der anorganischen Chemie; The Elements of Physical Chemistry; Handbuch der Mineralchemie; A Laboratory Manual of Qualitative Analysis for Students of Medicine, Dentistry and Pharmacy; <i>Traité Complet d'Analyse Chimique appliquée aux essais industriels</i> ; Der Nachweis organischer Verbindungen. Ausgewählte Reaktionen und Verfahren; Applied and Economic Botany; Chemistry of Common Things; Lehrbuch der physikalischen Chemie; Die Wasserstoffionenkonzentration... | 665 |

April.

General, Physical and Inorganic.

| | |
|---|-----|
| T. W. Richards and F. O. Anderegg: The Complications at the Anode in the Silver Coulometer (Voltmeter)..... | 675 |
| Edward W. Washburn and Earl B. Millard: The Ionic Hydration and Transference Numbers of Caesium Chloride..... | 694 |
| Emil O. Ellingson: The Heat of Neutralization of Hydroxylamine and Tetramethylammonium Hydroxide..... | 699 |
| Roger F. Brunel: A Criticism of the Electron Conception of Valence..... | 709 |
| George McPhail Smith: A Method for the Calculation of the Hydration of the Ions at Infinite Dilution, and the Ideal Diffusion Coefficient as Applied to the Hydrodiffusion of Electrolytes..... | 722 |
| Jnanendra Chandra Ghosh: The Influence of an Alternating Current on Electrolysis by a Direct Current..... | 733 |
| Grinnell Jones and Miner Louis Hartmann: Properties of Silver Iodide Interpreted in Relation to Recent Thermodynamics Conception..... | 752 |
| E. J. Shaeffer, M. G. Paulus and Harry C. Jones: Radiometric Measurements of the Ionization Constants of Indicators..... | 776 |
| L. M. Dennis and F. H. Rhodes: The Fractional Crystallization of the Picrates of the Rare Earths of the Didymium Group..... | 807 |
| T. W. B. Welsh and H. J. Broderick: Anhydrous Hydrazine. III. Anhydrous Hydrazine as a Solvent..... | 816 |
| T. W. B. Welsh and H. J. Broderick: Anhydrous Hydrazine. IV. Chemical Reactions in Anhydrous Hydrazine..... | 825 |
| George W. Sears and Clarence W. Balke: The Atomic Weight of Tantalum..... | 833 |
| W. B. Hicks: Solubility of Mixtures of Sodium and Potassium Chlorides in Solutions of Hydrochloric Acid..... | 844 |
| Edward C. Franklin: Ammonobasic Aluminium Iodides..... | 847 |
| Edward C. Franklin: Potassium Ammonoargentate..... | 852 |

Organic and Biological.

| | |
|---|-----|
| Harry Shipley Fry: Interpretations of Some Stereochemical Problems in Terms of the Electronic Conception of Positive and Negative Valences..... | 855 |
| J. M. Johlin: A Method for the Separation and Identification of Certain Homologous α -Diketones..... | 892 |

| | |
|--|-----|
| G. A. Burrell and I. W. Robertson: The Separation of Ethane and Ethylene by Fractional Distillation in a Vacuum at Low Temperatures..... | 896 |
| R. M. Isham and C. E. Vail: On the Oxidation of Ether..... | 902 |
| William McPherson and George Weatherworth Stratton: A Contribution to the Study of the Constitution of the Hydroxyazo Compounds. The Action of Unsymmetrical Benzoylparatolylhydrazine upon Benzoquinone and Its Homologs..... | 906 |
| C. A. Jacobson: Cicutoxin: The Poisonous Principle in Water Hemlock (<i>Cicuta</i>). .. | 916 |
| J. R. Bailey and D. F. Snyder: A New Synthesis of Iminoacetoneitrile and Its Conversion to Hydrazinodiacetic Acid..... | 935 |
| J. R. Bailey and D. F. Snyder: The Nitroso Derivatives of Semicarbazinodiacetic Acid Esters..... | 942 |
| Jokichi Takamine, Jr.: A Study of the Ninhydrin Reaction in Relation to the Age and Habits of Individuals..... | 946 |
| New Books: A Laboratory Manual for the Detection of Poisons and Powerful Drugs; Kurzes Lehrbuch der Organischen Chemie; An Introduction to the Study of Organic Chemistry..... | 949 |

May.

General, Physical and Inorganic.

| | |
|--|------|
| Frederick H. Getman and Vernetta L. Gibbons: The Reproducibility of the Cadmium Electrode..... | 953 |
| Joel H. Hildebrand: The Entropy of Vaporization as a Means of Distinguishing Normal Liquids..... | 970 |
| E. C. C. Baly: A Theory of Chemical Reaction and Reactivity..... | 979 |
| Theodore W. Richards and Frederick Barry: The Heats of Combustion of Aromatic Hydrocarbons and Hexamethylene..... | 993 |
| Gregory Paul Baxter and Thorbergur Thorvaldson: A Revision of the Atomic Weight of Lead. The Analysis of Lead Bromide..... | 1020 |
| Gregory Paul Baxter and Fred Leslie Grover: A Revision of the Atomic Weight of Lead. The Analysis of Lead Bromide and Chloride..... | 1027 |
| Gregory Paul Baxter and Merritt Roy Grose: The Vapor Pressure of Iodine between 50° and 95°..... | 1061 |
| M. A. Rosanoff, John F. W. Schulze and R. A. Dunphy: On Fractional Distillation with Regulated Stillheads..... | 1072 |
| Edgar J. Witzemann: A New Method of Preparation and Some Interesting Transformations of Colloidal Manganese Dioxide..... | 1079 |
| W. A. Withers and Alex. L. Feild: A Conductivity of the Study Reaction between Calcium Nitrate and Dipotassium Phosphate in Dilute Solution..... | 1091 |
| J. W. Turrentine: The Behavior of Certain Hydrazine Salts on Decomposition by Heat..... | 1105 |
| J. W. Turrentine and J. M. Olin: Electrochemical Oxidation of Hydrazine Sulfate and Ammonium Hydroxide..... | 1114 |
| J. W. Turrentine: A Description of the New Compound, Hydrazine Diperchlorate..... | 1122 |
| Franklin C. McLean and Donald D. Van Slyke: A Method for the the Titration of Small Amounts of Halides..... | 1128 |
| Reginald S. Dean: The Oxidation of Sulfides with Potassium Iodate..... | 1134 |
| J. M. Lindgren: The Determination of Boron in Iron..... | 1137 |
| Irving Langmuir: Chemical Reactions at Low Pressures..... | 1139 |
| Lloyd C. Daniels: Cuprous Salts of Oxygen Acids and a New Method of Preparing Cuprous Salts..... | 1167 |

| | |
|---|------|
| Sara Stowell Graves..... | 1171 |
| Leason H. Adams: The Use of the Interferometer for the Analysis of Solutions..... | 1181 |
| P. B. Davis and Harry C. Jones: The Viscosities of Binary Mixtures of the Associated Liquids, Water, Formic Acid and Acetic Acid..... | 1194 |
| Notes: Some New Forms of Apparatus: I. A Substitute for the Twin-bulb Trap in Toluene—Mercury Thermoregulators. II. A New Form of Pycnometer for Liquids..... | 1198 |
| Corrections..... | 1200 |

Organic and Biological.

| | |
|---|------|
| W. R. Orndorff and E. R. Allen: The Orcinolphtaleins, the Orcinoltetrachlorophtaleins, and Some of Their Derivatives..... | 1201 |
| Lambert Thorp and E. R. Brunsell: <i>o</i> - and <i>p</i> -Chlorobenzoylactic Esters and Some of Their Derivatives..... | 1258 |
| C. S. Hudson and J. K. Dale: A Comparison of the Optical Rotatory Powers of the Alpha and Beta Forms of Certain Acetylated Derivatives of Glucose.... | 1264 |
| C. S. Hudson and J. M. Johnson: The Isomeric Octacetates of Lactose..... | 1270 |
| C. S. Hudson and J. M. Johnson: The Isomeric Alpha and Beta Octacetates of Maltose and of Cellose..... | 1276 |
| C. S. Hudson and J. K. Dale: The Isomeric Pentacetates of Mannose..... | 1280 |
| C. S. Hudson and D. H. Brauns: Crystalline <i>d</i> -Fructose Pentacetate..... | 1283 |
| Emerson R. Miller and Jemison Mims Moseley: The Volatile Oils of the Genus <i>Solidago</i> | 1285 |
| Fred W. Upson and J. W. Calvin: On the Colloidal Swelling of Wheat Gluten.. | 1295 |
| H. C. Sherman and M. D. Schlesinger: Studies on Amylases. X. Comparison of Certain Properties of Pancreatic and Malt Amylase Preparations..... | 1305 |
| Frank E. Rice: Studies on the Action of Erepsin..... | 1319 |
| J. H. Long: On the Physiological Activity of Combined Hydrochloric Acid.... | 1333 |
| L. F. Foster and P. B. Hawk: Gastro-intestinal Studies. VII. The Utilization of Ingested Protein as Influenced by Undermastication (Bolting) and Overmastication (Fletcherizing)..... | 1347 |
| Notes: A Convenient Apparatus for Chlorination with Phosphorus Pentachloride. The Condensation of Vanillin and Piperonal with Certain Aromatic Amines..... | 1361 |
| New Books: The Chemistry of the Radio-Elements. Oedema and Nephritis. A Critical, Experimental and Clinical Study of the Physiology and Pathology of Water Absorption in the Living Organism..... | 1364 |

June.

General, Physical and Inorganic.

| | |
|---|------|
| William D. Harkins and Ernest D. Wilson: The Changes of Mass and Weight Involved in the Formation of Complex Atoms..... | 1367 |
| William D. Harkins and Ernest D. Wilson: The Structure of Complex Atoms. The Hydrogen-Helium System..... | 1383 |
| William D. Harkins and Ernest D. Wilson: Recent Work on the Structure of the Atom..... | 1396 |
| Stuart J. Bates: Osmotic Pressure and Concentration in Solutions of Electrolytes and the Calculation of the Degree of Ionization..... | 1421 |
| Duncan A. MacInnes and Karr Parker: Potassium Chloride Concentration Cells..... | 1445 |
| J. Livingston R. Morgan: The Drop Weight Method for the Determination of the Surface Tension of a Liquid..... | 1461 |

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

THE DEVELOPMENT OF CHEMICAL RESEARCH IN AMERICA.¹

By IRA REMSEN.

Received November 9, 1914.

Our main object this evening is to do honor to the memory of Josiah Willard Gibbs. We owe to the generosity of Mr. William A. Converse the opportunity to come together for this purpose and for the further purpose of witnessing the award of the Willard Gibbs Medal. That I have been honored by the Chicago Section of the American Chemical Society in being selected as the recipient of the medal this year gives me much satisfaction and pleasure and I desire to thank you one and all for this marked evidence of your good will and good opinion. I should prefer to divert your attention from myself and my contributions to our science, and to devote my address to a presentation of the work of Willard Gibbs, who is the real guest of honor this evening, for he is surely present in spirit. I may as well confess, however, that I do not feel competent to discuss his work. I have, to be sure, studied it and gained some knowledge of it, but I have not mastered it, and have not, therefore, reached a stage in which it has become a part of my mental machinery. I do not think in terms of the phase rule. Probably I was born too early in the last century.

On the other hand, I knew Gibbs, though not intimately. In the early

¹ Abstract of an address before the Chicago Section of the Society on the occasion of the award of the Willard Gibbs Medal, May 15, 1914. The address was not written and the writer has had to rely largely upon his memory.

days of the Johns Hopkins University, in the academic year 1879-80, he gave a course on Theoretical Mechanics for the students of that university. As I was then a professor there, I necessarily met him frequently, and it has always been a source of gratification to me that I was permitted to know, even if not intimately, one whose work has shed so much luster upon the science of this country. I remember him very well, for even then, only shortly after the publication of his great memoir on the Equilibrium of Heterogenous Substances, those who were especially interested in scientific research in America looked up to him and hailed him as a leader, though many years were to pass before the world at large recognized in him one of the greatest and most original thinkers of his time.

I congratulate Mr. Converse upon his happy thought of calling a medal after this great man, and I congratulate you, members of the Chicago Section, upon the opportunity this act of Mr. Converse has given you of coming together to honor his memory.

In accepting the medal I have also accepted the obligation to address you upon some subject of interest to chemists and I have chosen as my subject "The Development of Chemical Research in America."¹ In the time at my disposal I shall not, of course, be able to do full justice to the subject, but I hope to be able to call your attention to the more important facts that mark the course of this development. I want, if possible, to point out the conditions under which research developed and became what it is today—epidemic. It was sporadic for many years, but it later became epidemic and is now, in fact, in a most acute stage.

There was not much research in this country in the eighteenth century. This is not surprising, for there were many other things to do. We were busily engaged in trying to make a nation and in developing our material resources. Nevertheless, during the last part of the eighteenth century there were a few who tried their hand at chemical research, and at the beginning of the nineteenth century a fair start was made.

In 1794 one of the great chemical workers of the time, Priestley, the immortal discoverer of oxygen, came to this country and settled at Northumberland on the Susquehanna River in Pennsylvania. He was in correspondence at that time with the authorities of the University of Pennsylvania, and he was also in correspondence with Jefferson into whose brain the germ of the University of Virginia had found its way. I mention Priestley because he was the first distinguished chemist in this country, but his work here did not have much effect on chemical research, for he devoted his attention almost wholly to theological questions.

¹ While I was engaged in collecting data for this address, Edgar F. Smith's "Chemistry in America" appeared, and I gladly acknowledge my indebtedness to this book.

The strongest scientific influence here at the time of which I am speaking was that of Franklin. He had produced a deep impression upon a group of people in Philadelphia, and this city became the chief center of scientific activity. For some time afterwards the leading chemists of America were those who came from that city. Among these the most prominent was Robert Hare. From all that I can gather from his writings he was really a very remarkable man. When he was but twenty years old he invented the compound blowpipe. That was a noteworthy achievement for a young man of twenty. It required a good deal of courage, ingenuity, and perseverance to devise such an apparatus. The compound blowpipe has been of great importance to science and industry. Some years ago I became interested in the double halides and published an article giving my views regarding the nature of these compounds. Soon after the appearance of my article I received a letter from Dr. Wolcott Gibbs telling me that Robert Hare had expressed similar views in 1821. He sent me his copy of Hare's *Chemistry* and I was astonished to read the chapter that had been written fifty or sixty years before my article. The line of thought was practically identical with mine, and it was expressed beautifully. Now, that man was active in Philadelphia from 1801 to 1847, during which time he was professor of chemistry in the University of Pennsylvania. He was both investigator and scientific philosopher.

Following Hare came Robert E. Rogers (1813-1884), James C. Booth (1810-1888), and T. Sterry Hunt (1826-1892). Hunt was an extensive experimenter and a prolific writer, and throughout his life exerted a marked influence upon chemical research in America. A contemporary of Hunt was John Lawrence Smith (1818-1883), who was also an enthusiastic investigator in the field of chemistry. In this connection should be mentioned the method he devised in 1853 for decomposing alkaline silicates by the use of calcium carbonate and chloride—now in general use. He left a considerable fortune, and some of it, as a trust fund, came to the National Academy of Sciences for the purpose of aiding and encouraging researches on meteorites.

We come now to two men who stood out very prominently as investigators. I remember when, in my youth, I became interested in chemistry I frequently heard their names, but what they investigated or why they investigated it I did not know. I refer to Wolcott Gibbs (1822-1908) and Frederick A. Genth (1820-1893). Gibbs was one of the highest-minded men I have ever known. He never wavered in his loyalty to science, and was true to his convictions to his last days. I visited him in Newport about two years before his death, when he was eighty-four years old. He took me out to his private laboratory—he had retired from active service at Harvard some years before that—and there he talked enthusiastically of work he had in mind for the future. It was an inspiration to

be with him. His influence on the development of chemical research in America cannot be overestimated.

Genth was of a different type. He was an able man, and a good, jolly German. He came to this country about 1848, and established a commercial laboratory. During the early years of his residence he and Gibbs, working together, carried out an elaborate investigation on the cobalt ammonia bases, in the course of which they brought to light a large number of complex compounds that proved to be of interest, and set many chemists to thinking. Now, I am almost inclined to say that the chief value of that work at that time was to be found in the fact that it impressed upon the minds of young American chemists the idea of the possibility of creative work in chemistry. What it was all about many of us did not know, but it fired our imagination and furnished us an ideal. I am sure that it had a marked influence for good upon many young men, and was a strong force among those that helped the development of chemical research among us. Genth afterward became professor of chemistry in the University of Pennsylvania in 1872 and continued active work to the end of his life.

Josiah Parsons Cooke (1827-1894), who was professor of chemistry at Harvard from 1850 to his death in 1894, was another of the six prominent chemical investigators whose influence was, and is, widely felt. He began research work early in his career and continued it to the end. It is interesting to note that he was entirely self-taught as a chemist. The work of his last years had largely to do with atomic weights.

Then there was Samuel W. Johnson, of Yale (1830-1909), whose influence was felt in the field of agricultural chemistry, and John W. Mallet (1832-1912), who worked at the University of Virginia and helped to keep the spirit of research alive. In this connection, we should also recall the name of M. Carey Lea (1823-1897), who, under great difficulties, held a true course. He had his own laboratory and had no students, so that his influence was perhaps not as great as it undoubtedly would have been if he had been in a position to found a school.

From what I have said it is evident that there was no time in the first half of the last century when chemical researches were not in progress in this country, but still the total result was small in comparison to the number of chemists. In 1872, when I began to study the conditions, I was surprised to find how few centers of activity there were in America and, on the whole, how little was being done. I had just returned from a residence of five years in Germany where I had devoted myself to the study of chemistry and had made a modest beginning in research. The life of the chemical investigator appealed to me very strongly as it has to many others. I was, in fact, fascinated by it, and my highest ambition was to secure a place where I could live that life. But there were few such places in America

at that time and they were filled. One of the first things that offered itself was a professorship of physics and chemistry in Williams College. That I accepted a place calling for a knowledge of physics shows that I had some courage. I am very glad I went there and had four years' experience in a college of that kind. I made lifelong friends and became familiar with an American college, and altogether the experience was one which I prize highly, but looking at it from the point of view of my scientific ambitions it was most discouraging. I did, however, secure a small room which I fitted up as a laboratory and, in solitude, I did a little work. There were times when it seemed as though I should give up, and settle down into a routine teacher. There was very little sympathy for my work. I remember that once just after the appearance of one of my first articles in the *American Journal of Science*, we had a faculty meeting in the college library. Someone picked up the number of the journal containing my article and some good-natured fun was poked at me when an attempt was made to read the title aloud. I felt that in the eyes of my colleagues I was rather a ridiculous object. But I was only about twenty-seven and perhaps a little oversensitive.

The Johns Hopkins University was opened in 1876 and early in that year I was offered the professorship of chemistry. It would be difficult, not to say impossible, for any one who has not had the same experience to form any conception of the hope and joy that came to us young men in the message from President Gilman that in the new university an effort would be made to provide for the needs of those who wished to carry on researches. Here was an opportunity of which many had been dreaming. It is needless to say that I accepted the offer with alacrity. President Gilman's injunction was simply this: "Do your best work in your own way." What could be finer? I bought all the apparatus I wanted and all the books I wanted. A simple laboratory was built. I had but three or four students and we went to work. Now, I am well aware of the fact that chemistry was not revolutionized as a result of our efforts, but we made a start in a new direction. Research became an essential part of the training of graduate students and soon they began to come in larger and larger numbers. There was great enthusiasm among these students. I have often been surprised and delighted to see how, generally, advanced students of chemistry (no doubt it is the same with other subjects) become deeply interested in the most abstruse problems the moment they begin to feel that what they are doing is going to be a contribution, even though a slight one, to the knowledge of the subject.

Soon another step was taken of necessity. After we had been working for about a year the question of publication presented itself. I had up to that time been sending my occasional articles to Professor James D. Dana for publication in the *American Journal of Science*, but now the

amount of material sent by me evidently frightened the editor, and in a short time my manuscript was returned with the statement that it would be necessary to find some other place to publish my articles, as they seemed too highly specialized and too voluminous for a journal of general science. Professor Dana very kindly suggested that I start a journal myself. After corresponding with the leading workers in chemistry with discouraging, as well as encouraging, results, I decided to act upon the suggestion, and early in 1879, thirty-five years ago, the first number of the *American Chemical Journal* was issued. For a number of years that journal contained the principal original contributions to chemistry that came from this country. It flourished far beyond my expectations, but within the last few years it became evident to me that the journal of our society was coming more and more to be looked upon by American chemists as the best medium of publication of their contributions and, somewhat reluctantly and with a sacrifice of sentiment, in January, 1914, I transferred my journal to the tender mercies of the society in full confidence that the interests of American chemists would, on the whole, be better served by consolidation than by separate existences. I think it probable that the *American Chemical Journal*, especially during the early years of its existence, exerted a stimulating influence upon chemical research in America, but no one can measure this influence, and it is perhaps idle to refer to it as a possible factor. Whatever the influences may have been that led to increased activity in chemical research in this country, it is certain that the increase was very marked soon after the time of which I have just been speaking. This was due, I think, largely to the fact that such excellent opportunities were given the little band of workers at Johns Hopkins. This led to similar opportunities being given to the workers in other institutions, and many of these profited greatly in consequence. It was not long before there were a number of centers of activity in America, and the number of those devoting themselves to research work has increased astonishingly. It is not necessary for me to speak in detail of the splendid work done at Harvard under the leadership of Hill and Jackson and Michael and Richards; of A. A. Noyes and his co-workers at the Massachusetts Institute of Technology; of Chittenden, and Wheeler, and Treat B. Johnson at Yale; of Bogert and Alexander Smith at Columbia; of Edgar F. Smith at the University of Pennsylvania; of Morse and Abel and Jones at Baltimore; of Bancroft and Orndorff at Cornell; of Gornberg at Michigan; of Nef and Stieglitz at Chicago; of W. A. Noyes at Illinois; of the group at Wisconsin; and those at California and Leland Stanford. The world is familiar with these names and the work they stand for. There are many other workers in the field. It would be a pleasure to me to mention them all. Now that I am to be counted among the old men of the day I may be permitted to express my great satisfaction

at the changes for the better that have taken place within my life time. Chemical research is in a healthy condition in our country and the signs of future growth are most promising. May I add in conclusion that, though circumstances have kept me out of the field of chemical work for some years past, I now see my way clear to entering that field again, and I can think of nothing that could give me greater pleasure than the prospect of taking up the work in chemistry that I had to abandon thirteen years ago. It is a little late for me to begin again, but I believe that I shall yet be able to experience some of the joys that came to me so abundantly in the past while struggling with my old, inanimate laboratory friends. The transformation from university president to chemist is complete, and I rejoice.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE INCLUSION OF ELECTROLYTE BY THE DEPOSIT IN THE SILVER VOLTAMETER.

By T. W. RICHARDS AND F. O. ANDERREGG.

Received October 31, 1914.

I. Introduction.

The silver voltameter (or better, coulometer) is an instrument of such great importance in the exact measurement of the electrical quantity that its study by many investigators is highly desirable; therefore, the widespread attention which it has received during recent years is gratifying.

Since the classical researches of Lord Rayleigh and Mrs. Sidgwick¹ and F. and W. Kohlrausch,² carried out between 1880 and 1883, the subject has been studied in many places and from many points of view. The earlier of these investigations are mentioned in detail in the description of a protracted research carried out at Harvard University, and published years ago by one of the present authors in conjunction with two assistants.³ More recently the National Bureau of Standards, at Washington, the National Physical Laboratory, at Teddington, near London, England, and the Physikalisch-Technische Reichsanstalt, at Charlottenburg, Berlin, as well as other independent physical chemists, have conducted elaborate investigations concerning the nature of several irregularities in this instrument.

The most careful of these researches have verified the main calculations

¹ *Phil. Trans.*, (A) **175**, 411 (1884).

² *Wied. Ann.*, N. F., **27**, 1 (1886).

³ Richards, Collins and Heimrod, *Proc. Am. Acad.*, **35**, 123 (1899); Richards and Heimrod, *Ibid.*, **37**, 415 (1902); also *Z. physik. Chem.*, **32**, 321 (1900); **41**, 302 (1902).

brought forward in the earlier research conducted at Harvard; but unanimity has not yet been attained with regard to all the details.

Much time has been spent upon the question as to the purity of the electrolyte and the cleanliness of the apparatus, especially the porous cup recommended in the Harvard researches. These investigations were important perhaps from the standpoint of the average chemist, or especially that of the physicist unused to working with pure material, but there seems to be no important point (except perhaps the precise effect of acidification) in all this part of the recent work which was not appreciated at Harvard, fifteen years ago. Any one who has worked much upon atomic weights dealing with silver nitrate solutions would think of contaminating such a solution with organic material of any kind, especially filter paper; and there is no question that the silver nitrate used in the early Harvard work satisfied all the necessary requirements of the more recent critics. Moreover, it is obvious that a porous cup (if one is used) must be thoroughly washed free from either acid or alkali immediately before use. These patent facts might perhaps have been more emphasized instead of having been assumed almost as a matter of course, in the early Harvard papers; and if this had been done, time and trouble on the part of others might have been spared; the essential precautions were recognized long ago.

About the importance of pure materials, chemically clean apparatus, and electrically perfect insulation, there can thus be no doubt that all authorities are now agreed, the very recent work having emphasized the earlier conclusions; but concerning certain other irregularities of the silver voltameter, as has been said, there seems to be a real difference of opinion. Some of the investigators seem to think that organic impurity in the electrolyte is the *only* cause of excessive deposits on the cathode. That it is *one* of the causes there is no doubt; but it is equally clear to us that there are others. It is with regard to these points, especially, that the present work was undertaken.

The points in dispute concern in the first place the existence or non-existence of included mother liquor in the crystals deposited upon the cathode; secondly, the nature of the mother liquor (if any) thus included; thirdly, the existence or nonexistence of a surplus of silver in the liquid flowing from the anode; and fourthly, the efficacy of a porous cup as a means of promoting exact coulometric work through the separation of the anode and the cathode.

The present paper considers the first two of these points, *viz.*, those which concern the included mother liquor. It was necessary to settle these before any conclusive evidence concerning the other two could be obtained; for the decision depends largely upon small differences in weight of the precipitated silver crystals, and these differences might either be caused or be masked by differences in the amount of mother liquor included.

The experiments in the three national physical laboratories seem to have underrated the importance of this point, while exerting very praiseworthy care in other directions.

The first investigators to call attention to this very important source of error caused by inclusion of electrolyte were Lord Rayleigh and Mrs. Sidgwick. They determined the extent of the inclusion chiefly by heating the crystallized silver just short of redness. Their results showed that in many cases the inclusion of mother liquor unquestionably takes place; moreover, there could be no question that its amount varied according to circumstances. New solutions yielded less inclusion in the crystals than the old ones, and large crystals less than small ones.

These results were entirely verified by the Harvard work carried out many years afterwards.¹ The magnitude of the inclusion was found to vary from 0.003 to 0.03% from loss of weight on heating, and an average case was verified by analysis. The experience with silver crystals has been supported by plentiful experience with other kinds of crystals in the course of the Harvard work upon the atomic weights. Indeed, it is not too much to say that we have never been able to obtain crystals of any kind free from traces of mother liquor, although, of course, the amount included varies greatly according to the details of crystallization.²

In spite of this experience, Gray³ and van Dijk⁴ denied the existence of such included mother liquor, and Smith, Mather and Lowry have supported these doubters,⁵ as well as Jaeger and von Steinwehr.⁶ A study of these papers, however, shows that either the accuracy of the work was not adequate, or else the heating was not carried far enough to prove the point. Unquestionably, van Dijk and Smith, Mather and Lowry in most cases failed to use a temperature sufficiently high to drive off the inclusions and probably this was the case also with Jaeger and von Steinwehr. Attention has already been called to the need of heating the silver to so high a point that the metal has become somewhat softened.⁷ The mother liquor is then set free by a series of small explosions or decrepitations, and the temperature needed is over 550°. It is quite possible, indeed, that the last traces of included matter are not expelled until the silver is completely fused,⁸ but very nearly all of it is driven out at dull redness,

¹ Richards, Collins and Heimrod, *Proc. Am. Acad.*, **35**, 123 (1899).

² Richards and Heimrod, *Ibid.*, **37**, 415 (1902); Richards, "The Inclusion and Occlusion of Solvents in Crystals," *Proc. Am. Phil. Soc.*, **42**, 28 (1903); *Z. physik. Chem.*, **46**, 189 (1903).

³ *Phil. Mag.*, [5] **22**, 389 (1886).

⁴ *Ann. d. Phys.*, **14**, 569 (1904); **19**, 249 (1906).

⁵ *Phil. Trans.*, (A) **207**, 545 (1908).

⁶ Jaeger and von Steinwehr, *Z. f. Instrumentenk.*, **28**, 327, 353 (1908).

⁷ Richards, *Proc. Am. Acad.*, **44**, 91 (1908).

⁸ Richards, *Proc. Am. Phil. Soc.*, **42**, 28 (1903); *Z. physik. Chem.*, **46**, 189 (1903). Hulett has confirmed this inference.

as we have repeatedly shown. In discussing their experiments on this point, Jaeger and von Steinwehr make a somewhat incomprehensible correction for loss of weight of the crucible during heating. A clean platinum crucible, in our experience, heated to a temperature below redness, does not usually lose an important amount in weight, although they applied such a correction. If this doubtful correction were omitted, their results tend to confirm ours.

The recent work carried out by the Bureau of Standards seems not to have heeded sufficiently the inclusion of mother liquor, in spite of the arguments previously presented concerning it. More recently results which have been obtained by Hulett in careful collaboration with Duschak and with Laird¹ have entirely confirmed the conclusions of Lord Rayleigh, which had indeed been thoroughly verified at Harvard long before the Princeton work was begun. Hulett and his collaborators adopted van Dijk's somewhat questionable preliminary operation of scraping the crystals from the platinum dish. This is necessary, if the crystals are to be heated in a tube, but it has one important disadvantage, namely, that this forcible treatment of the crystals might very well open cells containing mother liquor which would otherwise remain closed, especially cells between the crystals and the platinum cathode. In his later work with Laird, Hulett used melted tin as a solvent for the silver; but one cannot help thinking, especially because of the large amount of carbon dioxide which he found, that dust had, during some stage of the operation, found its way into the tube. Neither of these methods (although each gives interesting results) seems to provide exactly the information desired, namely, the weight of the inclusions actually held by the deposit as weighed.

The attempt to determine the inclusions by attacking the silver deposit with mercury, as practised by the Bureau of Standards,² is likewise of uncertain value, because the solubility of silver in mercury is very slight (as we have found by careful experiment³) and the metal is merely converted into a solid amalgam which might withhold some of the included impurities.

For these reasons it is not necessary to discuss more fully here the interesting details of all this recent work. The very careful researches of Hulett and his collaborators substantiate that previously carried out at Harvard in showing, first, that the inclusions are often important in amount, and secondly, that they vary considerably according to the details of experimentation. Thus, for an accurate determination of the weight of

¹ Hulett and collaborators, *Trans. Am. Electrochem. Soc.*, **12**, 257 (1907); **22**, 345 (1912).

² Bur. Standards, *Bull.* **10**, 520 (1914).

³ See also Reinders, *Z. physik. Chem.*, **54**, 609 (1906). A saturated liquid amalgam at 20° contains only 0.04% of silver.

metallic silver deposited by the current the amount of inclusion must be determined in each experiment.

Nevertheless, it seemed desirable to institute new experiments touching the more essential points involved. In the course of these experiments, the weight of silver chloride obtained from the coulometric deposits was compared with the weight of silver chloride obtained from perfectly pure silver. This gives theoretically the most conclusive method of determining the amount of the impurity, but is, of course, difficult of execution. Again, crystals were ignited at high temperatures and care was taken to find the point at which constancy of weight was attained, and also the point at which appreciable volatilization of the silver began to invalidate the result. Yet further, a number of deposits were scraped from their cathodes à la van Dijk and Hulett. Both crystals and cathode were washed with pure water before ignition, and it was thus found that cells containing silver nitrate solution had really been opened up by the scraping. The analyses of these crystals pointed to the same conclusion. Finally, methods for determining the amounts of inclusion having been settled, comparisons were made of the extent of inclusion involved in the various forms of the coulometer. These experiments are set forth in detail below. One does not see how any candid or unprejudiced reader, however he may have felt with regard to previous contributions on this subject, can escape the inference that inclusions in silver crystals are really important and that no coulometric work is complete until the amount which pertains to the particular method employed is discovered by actual analysis.

II. Details Concerning the Apparatus.

The porous cup coulometer as used consistently throughout this research as a standard instrument was precisely similar to that recommended by one of us in connection with G. W. Heimrod, twelve years ago.¹

A large platinum crucible with a lip, weighing about 60 g. and containing about 120 cc. was used to contain the catholyte. In it was suspended from a glass arm a small porous cylindrical Pukal cup which contained the anolyte, always kept at least 1 cm. in level below the catholyte. Everything was thoroughly insulated by glass and paraffin, and the whole was arranged under a bell-jar to protect from dust or outside impurity. The inner level was maintained constant either by a constant level siphon or by a pipet. The anodes consisted of metal carefully prepared in a pure state according to the usual method,² fused in hydrogen on lime in the electric furnace. They were scraped with pure sea-sand and etched with pure dilute nitric acid. In a few cases they were plated with additional silver electrolytically. The porous cups were, of course,

¹ *Proc. Am. Acad.*, **37**, 415 (1902); *Z. physik. Chem.*, **41**, 302 (1902).

² See Richards and Wells, *THIS JOURNAL*, **27**, 481 (1905).

thoroughly digested with nitric acid and then boiled with repeated portions of the purest water until every trace of acid had been washed from their pores. In the crucial portion of the work this was done after every experiment.

The nitric acid used throughout the work was always the middle third, carefully redistilled, of an acid already very pure.

The silver nitrate used as electrolyte was prepared either from silver made according to the method of Stas, or in the later experiments from silver precipitated by acidified ammonium formate. The salt was always crystallized twice, the first time from a slight excess of nitric acid and the second time from pure water, a trace of acid remaining in the mother liquor from the previous crystals. This method provides, as the work of the Bureau of Standards has shown, a solution which is free from basic salt. In some cases also solutions which had already been used in the coulometer were filtered through asbestos and then recrystallized three times, the first two times from 10% acid and the final time as before without adding any acid. Each batch of crystals was centrifuged as usual. All the water used in the important parts of this research was purified by redistilling first from alkaline permanganate solution, and again from a trace of sulfuric acid.

For convenience in regulating the current, an ampere meter was included in the circuit. Unless otherwise stated a current of about 0.25 ampere was used in the work. After the electrolysis was completed, the porous cup was removed and the catholyte was siphoned into a small labelled crystallizing dish, leaving a few cubic centimeters of the solution in the bottom of the large crucible. The occasional loose crystals of silver which either remain at the bottom or float on the surface of the electrolyte are thus kept in the original vessel. The cathode vessel was then filled with pure water, which was immediately siphoned into a large labelled dish; and this process of washing was repeated several times at even greater intervals until evening, when the crucible filled with the purest water was allowed to stand over night. On the next morning this wash-water was tested in the nephelometer with sodium chloride against pure water, to see if all the accessible silver nitrate had been washed from the pores of the crystals. In all cases, except two, this wash-water was found to be free from silver nitrate, and in these two cases another change of water left till noon showed no traces of this salt. Finally the deposit was rinsed with very pure water, a few milliliters of which were left in the crucible. Any minute crystals of silver that may have passed over were recovered with a small platinum spatula. Our experience agrees with Hulett's, that a particle smaller than 0.01 mg. may be seen and recovered. The crucibles were heated two hours at 160°, after the water had been evap-

orated, in electric ovens, cooled and weighed as before with all the precautions for exact weighings.

A building with its temperature regulated by thermostats, a balance very free from vibration, and favorable conditions of every kind, were of great assistance in making accurate weighings of the cathode. The weighings were regularly duplicated to within 0.02 mg.

III. Inclusions Determined by Analysis.¹

After a regular double electrolysis (with two coulometers in series) had been made, the crucibles containing the weighed deposits were placed in large covered beakers nearly filled with warm water, and a slight excess of redistilled nitric acid was added. When the silver had been completely dissolved, the solution was quantitatively transferred to a two-liter precipitating flask. To the large bulk of solution an excess of very pure hydrochloric acid was gradually added—enough to precipitate all the silver—leaving dissolved an excess of ionized chlorine, in hundredth normal concentration.²

The precipitate was agitated till it had thoroughly coagulated, and allowed to stand in a dark room for twenty-four hours with occasional shaking; the filtering was done through a tared Gooch-Monroe crucible. The precipitate was washed ten times with wash water containing hundredth normal hydrochloric acid, being transferred to the crucible with the same wash water, and finally dried for five hours at 180–190°, cooled and weighed. The bulk of precipitate was then placed in a previously ignited porcelain crucible; and after weighing, the silver chloride was fused in a porcelain air bath. The fused mass was nearly colorless in all cases. Except silver chloride, the only substances present in this analysis are volatile, hence the process is an unusually precise one. A trace of silver chloride remaining in the precipitating flask was dissolved in a little ammonia, determined in the nephelometer, and added to the main weight.

The vacuum corrections for metal and halide are respectively, —0.031 mg. and +0.071 mg. per g. These were duly applied, and the calculation was carried out on the assumption that the atomic weights of the two elements are respectively, 107.880 and 35.459. The results are given in

¹ This method was tried once before at Harvard, the analyses having been made by Mr. E. Collins near the beginning of his part in the research (*Proc. Am. Acad.*, **35**, 139 (1899)). No claim was then made for great accuracy, but the outcome was in favor of a slight inclusion. The cause of the errors in Expts. 35 and 36 noted by Rosa (*Bur. Standards, Bull.* **10**, 518 (1914)) cannot now be traced, as the original notes are no longer accessible. In any case, the older analyses do not compare in authority with those given below.

² Forbes (*THIS JOURNAL*, **33**, 1937–1911) has shown that silver chloride is least soluble in such a concentration of chloride ions. Calculating from the solubility product (2×10^{-10}) it would take five liters of solution to dissolve 0.01 mg. of silver chloride, and hence no correction need be applied.

Table I; the table is easily comprehensible. For each of the last two analyses the products of the two coulometers were united for analysis. The calculated figures in the last column make allowance for the fact that the included mother liquor must have contained about 8 or 10% of silver nitrate, the silver in which must have been precipitated as chloride and weighed with that coming from the electrolytic metal.

TABLE I.—ANALYSIS OF ELECTROLYTIC SILVER DRIED AT 160°.

| No. of Expt. | Corrected wt. Ag. Grams. | Corrected wt. AgCl. Grams. | Calculated AgCl. Grams. | Diff. Mg. | Diff. in %. | Inclusions corrected for Ag as AgNO ₃ . Per cent. |
|--------------|--------------------------------|----------------------------------|-------------------------------|--------------|----------------|---|
| 20 | 2.79247 | 3.70988 | 3.71033 | 0.45 | 0.0121 | 0.0128 |
| 21 | 3.25640 | 4.32631 | 4.32674 | 0.43 | 0.0100 | 0.0106 |
| | 3.25644 | 4.32637 | 4.32680 | 0.43 | 0.0100 | 0.0106 |
| 22 | 2.66857 | 3.54521 | 3.54570 | 0.49 | 0.0138 | 0.0144 |
| | 2.66859 | 3.54531 | 3.54573 | 0.42 | 0.0118 | 0.0125 |
| 23 | 5.92000 | 7.86453 | 7.86585 | 1.32 | 0.0167 | 0.0176 |
| 24 | 5.72318 | 7.60322 | 7.604335 | 1.115 | 0.0147 | 0.0155 |
| Total | 26.28565 | 34.92083 | 34.925485 | 4.655 | 0.0133 | 0.0141 ¹ |

Evidently the actual weight of silver chloride found was always less than the theoretical weight. Hence the silver contained included impurity.

The quantity of inclusion thus found by direct analysis (0.014%) is close to that found by Richards and Heimrod, 0.018.² The present series of analyses determines this quantity by a method quite different from the old way.

In order to forestall the criticism that the deficiency thus found might simply be due to loss of silver during the analysis, very pure fused silver was prepared and analyzed with exactly the same precautions.

TABLE II.—ANALYSIS OF PURE FUSED SILVER.

| Corrected wt. Ag. Grams. | Corrected wt. AgCl found. Grams. | Calculated wt. AgCl. Grams. | Diff. Mg. | Diff. in %. |
|--------------------------------|--|-----------------------------------|--------------|----------------|
| 6.22211 | 8.26738 | 8.26725 | +0.13 | +0.002 |
| 5.16568 | 6.86361 | 6.86359 | +0.02 | +0.000 |
| 5.18476 | 6.88876 | 6.88893 | —0.17 | —0.002 |
| 16.57255 | 22.01975 | 22.01977 | —0.02 | 0.000 |

This result is very different from that previously found in the case of the crystallized electrolytic silver, and corresponds exactly with the value 35.459 for chlorine. The international value 35.460, also, is within the limit of experimental error. The evidence is very strong, therefore, that the analytical procedure was correct, and hence that the electrolytic silver prepared as we had prepared it, contains more than one part in ten thousand of included mother liquor.

¹ If Cl = 35.460, this value would be 0.0148%.

² *Loc. cit.*, p. 435.

III. Inclusions Determined by Heating the Deposits in the Cathode Crucible.

The ignition of the deposit for the purpose of determining the inclusions by loss of weight has been often used in the past, first by Lord Rayleigh and Mrs. Sidgwick, and later by many others. Some, trying to use it, have failed to heat the silver hot enough, as already stated.

In our experiments, after the crucible with its deposit had been washed, dried and weighed as usual, it was placed on a quartz triangle in a dark room. A clean porcelain crucible was inserted into the mouth to protect the material from dust and to cool and catch traces of silver vapor. The platinum was heated very carefully, with a burner held in the hand, until it attained dull redness, just barely perceptible in the dark. Great care was used to not exceed this temperature, and to heat the crucibles all over, as evenly as possible. The crucible was then cooled, and weighed once more.

Such heating slightly alloys the two metals; on dissolving the silver in nitric acid a perceptible amount of platinum remained. In preparation for a new trial, the inner surface was afterwards scrubbed, washing finally with acid and water. The crucibles lost a few tenths of a milligram each time, due to the removal of the platinum. Burnished crucibles suffered much less than those roughened by continuous use. This complication, of course, had not the slightest effect upon the quantitative experiment.

To settle the question raised by Jaeger and von Steinwehr, as to whether a platinum crucible alone loses weight when heated, one of ours was heated five times, just as if it had contained silver. The total loss was only 0.05 mg., or 0.01 mg. for each heating. This is negligible, but the corresponding correction was applied to each result for the sake of completeness.

The results concerning the amounts of included electrolyte found by heating the precipitated silver are summarized in Table III. Each figure is calculated from the actual loss on heating by adding to that quantity 6% of its value, to allow for the silver which must have remained from the included nitrate decomposed by heat. This will be explained more fully later. The first column records the amount of inclusion in silver precipitated on a crucible which had been somewhat scratched and roughened by van Dijk's process of mechanical removal of previous precipitates; the second column records the result for freshly burnished crucibles (both used as porous-cup coulometers); the third column gives the amount in an instrument according to Kohlrausch (the first four results coming from burnished crucibles and the last three from rough ones); the fourth column shows the increased inclusion when some of the anolyte is permitted to come into contact with the cathode deposit, and the last column shows the greatly increased effect when a large surface receives the silver crystals. The deposit varied in weight from 1.9 to 3.1 g. In order to be sure that no

silver volatilized during the ignition, the porcelain crucible which had been used as a cover during all the heatings was warmed with nitric acid; but no silver was found in this liquid on testing in the nephelometer.

TABLE III.--INCLUSIONS IN PRECIPITATED SILVER, FOUND BY HEATING.

(Expressed in fractions of per cent of weight of silver.)

| Porous cup roughened crucible. | Porous cup burnished crucible. | Kohlrausch form. | Cathode less protected from anode. | Porous cup, large cathode vessel (roughened). |
|--------------------------------------|--------------------------------------|---------------------|--|---|
| 0.0155 | 0.0076 | 0.0072 | 0.0218 | 0.0352 |
| 0.0134 | 0.0108 | 0.0061 | 0.0224 | 0.0311 |
| 0.0174 | 0.0097 | 0.0039 | | |
| 0.0194 | 0.0100 | 0.0115 | | |
| 0.0171 | 0.0100 | 0.0045 | | |
| 0.0174 | 0.0119 | 0.0055 | | |
| 0.0178 | | 0.0115 | | |
| 0.0125 | | | | |
| 0.0107 | | | | |
| 0.0139 | | | | |
| Av., 0.0155 | 0.0100 | 0.0083 | 0.0221 | 0.0332 |

These results are worthy of careful study.

In the first place, one notes that the average of the first column, including all the results obtained with the ordinary somewhat roughened porous cup voltameter, is 0.015—a figure close to that found by the actual analysis of the silver, 0.014, recorded in the last section, as well as to the earlier results found at Harvard and the still earlier work of Lord Rayleigh.

In the next place, it is clear that a roughened crucible considerably increases the inclusion, its figure being 0.015 instead of 0.010 found in the case of a burnished crucible.

Again, it is apparent from Column 5 that other things being equal, the inclusion is approximately proportional to the surface on which the silver is deposited—for the large platinum beaker-crucible used in this series had about twice the surface of the smaller vessel used for the experiments in Column 1, and the inclusion was about double. This surface effect is doubtless the real cause of the so-called "volume effect" noticed by various other experimenters,¹ for they failed to observe and correct for this greater occlusion which occurs on a larger surface. These figures give striking evidence of the importance of determining the amount of inclusion in each case, and by their final consistency strongly support the other work.

The surface-effect, producing greater inclusion, is doubtless also the reason why the Kohlrausch form of voltameter gave a lesser deposit; for in this form the receptacle placed under the anode to receive the "anode slime" cuts off nearly half of the cathode from usefulness, and the silver is actually deposited upon only a part of the platinum surface which would

¹ See for example Rosa, *Bull. Bur. Standards*, 9, 514 (1913).

be available in the porous-cup voltameter. This, of course, by increasing the current density, diminishes the practical maximum current strength which the instrument can safely endure, and makes a large crucible no more efficient than a small one would be with the porous cup.

Finally, it is evident from Column 4 that the anode impurities promote the inclusion, in confirmation of the Harvard work of 1900-1902 and of Hulett's later results.

Because, also, as the work at the Bureau of Standards has shown, by very extended experiments, both current density and temperature affect the size and distribution of the crystals, these factors also must affect the inclusion.

Evidently it is impossible to apply a correction so variable to any work upon this subject, either one's own or that of others, without an intimate knowledge of every detail. The only satisfactory method is to *determine with due precaution the amount of included electrolyte in every crystalline precipitate*; and no work in which this has not been done can possess final authority, at least as regards the exact weight of the precipitate.

IV. The Nature and Distribution of the Inclusion.

It is, of course, possible that the mother liquor included in the crystals is not of exactly the same composition as the original electrolyte. Around the cathode during active electrolysis the solution of silver nitrate is necessarily diluted; and the solution may be caught and imprisoned in this diluted condition.

A moment's thought will show, however, that the exact concentration of the imprisoned mother liquor is not a serious question. For example, if the total inclusion is 0.015%, a knowledge of the composition of the mother liquor within 7% would correspond to an accuracy of 1 part in 100,000 of the crystallized silver. This is a high degree of accuracy, which rarely needs to be exceeded. Supposing, therefore, that one starts with a 10% solution of silver nitrate, more than half of the dissolved substance might be eliminated without causing a serious effect upon the result. The error from any possible change of concentration is, therefore, less than the possible error which might be caused by scraping the crystals from the dish; for this process (as will be shown) allows water to evaporate from cells opened by abrasion. *The really important point, as usual, is to determine the amount of included water.*

On this account we have made no search as to the exact composition of the included mother liquor. The analyses made by Hulett seem to be more than sufficient for the purpose. Although variable, they indicate that the enclosed liquid under the conditions involved does not lose anything like as much as half of its dissolved salt.

As already stated, the presence of carbon dioxide, found by Hulett

in the gases obtained from the silver, is probably to be ascribed to dust, which doubtless furthers occlusion of mother liquor. No other reasonable source is assignable. At a high temperature this dust, even if protected from air, would burn in the oxygen of the nitric acid and be expelled. Obviously, therefore, the carbon would be eliminated from the final result, whether its weight were calculated from the amount found as a gas, or simply from the loss of weight of the heated silver. It is almost impossible to exclude such minute traces of dust under ordinary conditions; therefore, it is comforting to feel that in this case, at least, their influence is negligible.

One milligram of the original 10% electrolyte leaves 0.063 mg. of silver on ignition; and 8% solution would leave 0.051 mg. The cathode occlusions are probably between these limits, which are close enough for the purpose. Hence, to obtain the exact weight of the silver deposited electrolytically as metal, one must subtract from the weight of the precipitate ignited at a dull red heat about 6% of the loss on heating, as has been done above. As already stated, this is quite accurate enough. Incidentally, it may be stated, that a similar correction was thus applied in the early Harvard investigations.¹ For most purposes, where the weighings are not carried beyond 0.1 mg. the correction may be neglected altogether; the weight of the silver crystals heated to incipient redness may be taken directly as the weight of the metallic silver precipitated by the electrolysis.

The question concerning the distribution of the inclusion in the deposit is of more importance. Is the imprisoned liquid wholly in the body of the crystals, or is part of it held between the crystals and the platinum cathode? If the latter is the case, van Dijk's and Hulett's method of removing the crystals from the dish may open a part of the cells, allowing some of the liquid to evaporate; thus both the weight and concentration of the included solution may be wrongly estimated. This is a matter easily susceptible of experimental decision; and our study of it is recounted below.

In the first place, a number of deposits were prepared with the purest electrolyte and all the precautions already described. After most carefully washing, weighing and drying the deposit, each deposit was removed as far as possible from the platinum cathode with a platinum spatula. Both dish and spatula suffered somewhat, and the detached crystals of silver contained some platinum; but this did not affect the main point in question. The crystals were placed in a test tube and washed with a little water, which was then filtered through a Gooch crucible provided with quantitative asbestos. The cathode crucible was similarly washed, and its wash water similarly filtered. These wash waters were tested in the nephelometer by comparison with standard silver nitrate solution with every precaution.

¹ *Proc. Am. Acad.*, 37, 421 (1902); *Z. physik. Chem.*, 41, 308 (1902).

Table IV summarizes the results obtained with crystals deposited on cathodes somewhat roughened by this drastic treatment.

TABLE IV.—SILVER NITRATE CONTAINED IN THE WASH WATER FROM THE CRUCIBLES AND CRYSTALS.

| No. of Expt. | Deposit Ag in gms. | On crucible. mg. | On crystals. mg. | Total mg. | AgNO ₃ . %. |
|-----------------|-----------------------|---------------------|---------------------|--------------|---------------------------|
| 13 | 2.91711 | 0.025 | 0.037 | 0.062 | 0.0021 |
| | 3.00918 | 0.023 | 0.031 | 0.054 | 0.0018 |
| 14 | 2.73102 | 0.025 | 0.030 | 0.055 | 0.0020 |
| | 2.73097 | 0.028 | 0.024 | 0.052 | 0.0019 |
| 15 | 2.43529 | 0.011 | 0.018 | 0.029 | 0.0012 |
| | 2.43523 | 0.017 | 0.014 | 0.031 | 0.0013 |
| 16 | 3.19442 | 0.014 | 0.016 | 0.030 | 0.0009 |
| | 3.19439 | 0.026 | 0.012 | 0.038 | 0.0012 |
| Total, 22.64761 | | 0.169 | 0.182 | 0.351 | 0.00155 |

Thus, on the average, every gram of silver precipitated in this way enclosed 0.015 mg. of silver nitrate between the crystals and the dish. It remained to discover the amount of mother liquor imprisoned within the crystals themselves.

After drying these washed crystals for at least an hour at 160°, they were placed in a quartz crucible provided with a cover of the same material. When carefully weighed, they were heated in the flame of a Bunsen burner to dull redness. This heating was usually accompanied by a crackling sound, as the inclosed substances made their escape. The cooled crucible was weighed, and again heated, cooled and weighed as before until constant weight had been obtained.

The values obtained by this method gave a measure of the volatile matter in the crystals, which must be corrected for residual silver as before. In four determinations, 7.22 g. of silver lost 1.23 mg., or 0.017%. Corrected for residual silver from the enclosed nitrate, this becomes 0.018%.

Because of a fear lest some silver might have been lost by volatilization from the quartz crucible, the test was repeated, with a quartz test tube, fifteen centimeters long, in place of the crucible. In this test tube there were heated two portions of crystals which had been accumulated from several electrolyses, scraped from the crucibles and afterwards washed as before. To insure precision in weighing, a tare was used, consisting of a similar amount of silver which had already been heated in the crucible. A small tube of radioactive substance was kept in the balance case to remove any electrostatic charges from the tubes, and every precaution was taken to insure accuracy. During the ignition a thin-walled, cone-shaped glass tube was inserted well down into the top of the quartz tube, which was then inclined at an angle of 30–45° with the horizontal, and heated in a Bunsen flame. From this arrangement no trace of silver vapor could escape during the ignition. The inner glass

tube was duly tested for volatilized silver by treatment with nitric acid. In one case a trace was found, and due correction applied. In the second trial none was found.

When the silver had reached constant weight on successive treatings, the tube was evacuated with a water pump and again heated to see what effect the absence of most of the oxygen would have. Von Wartenburg¹ suggests the formation of silver oxide at high temperatures to explain the fact that silver is more volatile in oxygen than in an atmosphere of nitrogen or in a vacuum. The heating in the partial vacuum produced no perceptible effect on the weight. Two trials were made, using 10.1 and 9.8 g. of crystallized silver, respectively. The corrected losses of weight were 1.37 mg. and 1.12 mg. (or 0.0135 and 0.0115%), respectively. Averaging the results, we see that these specimens of washed silver contained 0.0125% of mother liquor. To this must be added the amount of silver nitrate which had been washed from their abraded surfaces, namely 0.00155 (see Table IV), making 0.014% in all. This is somewhat less than the loss of weight found in similar deposits when the crystals have not been removed from the dish (see Table III); hence it would appear that the removal of the crystals opens some cells which otherwise would remain closed at 160°, and allows the water to evaporate from the previously imprisoned silver nitrate. Hence it is clear that the method of van Dijk and Hulett is probably not an adequate way of determining the actual total amount of included mother liquor which is weighed with the crystals while the latter are still adhering to the dish.

Another very strong piece of evidence in support of these conclusions about the included mother liquor is to be found in the comparison of the final weights, after ignition, of deposits upon large and small coulometers in the same circuit. Whereas before heating the two gave very different results, after heating they were almost identical.

TABLE V.—WEIGHT OF DEPOSITS IN LARGE AND SMALL POROUS-CUP COULOMETERS.

| 1st Expt. | Weight after drying at 160°. | Weight after ignition at dull redness. | Final weight after cor. for residual Ag from AgNO ₃ . | Weight of included electrolyte. |
|-----------------------|------------------------------|--|--|---------------------------------|
| Large coulometer..... | 1.89559 | 1.89494 | 1.89490 | 0.00069 |
| Small coulometer..... | 1.89525 | 1.89492 | 1.89490 | 0.00035 |
| Difference..... | 0.00034 | 0.00002 | 0.00000 | 0.00034 |
| 2nd Expt. | | | | |
| Large coulometer..... | 3.13902 | 3.13812 | 3.13807 | 0.00095 |
| Small coulometer..... | 3.13868 | 3.13808 | 3.13805 | 0.00063 |
| Difference..... | 0.00034 | 0.00004 | 0.00002 | 0.00032 |

The second and third columns of figures show how nearly alike the results are after the ignition: that is to say, the apparently large difference

¹ *Z. Elektrochem.*, 19, 482 (1913).

between the results of the two sizes of coulometers (which would have been left unexplained as a "volume effect" if the methods of the three national bureaus had been used) is annihilated by the simple device of heating the crystals to a temperature high enough to drive off the included water.

In a recent able article by Bates and Vinal¹ appears the following statement: "The whole question of inclusions has been critically discussed by Rosa, Vinal and McDaniel.² Their opinion is that the deposits so perfectly crystalline as those formed from the purest silver nitrate do not contain significant inclusions." To us it seems that any such superficial evidence is far from convincing. One of us has shown repeatedly³ that no matter how beautiful a crystal, or how perfectly crystalline and transparent its structure may be, yet when it is crystallized from aqueous solution it is almost, if not quite, certain to contain some of the mother liquor, either in accidental submicroscopic cells or in "solid solution." Indeed, a careful review of this latest published comment, in the light of the foregoing experiments, fails to reveal any adequate argument against our conclusion.

V. The Purity of the Ignited Deposit.

Only one final question remained: is crystallized silver, which has been thus heated at a dull red heat, really pure silver? Upon this point the validity of the whole coulometric process depends. From the fact that the amount of inclusion as found by analysis agreed closely with that found by heating the silver, it is clear that the heated crystals must have been very nearly pure; but the matter was clinched by actual analyses of two of the specimens remaining from the work described on p. 20. On solution in nitric acid, each preparation was filtered through a Gooch-Munroe crucible with every quantitative precaution, and the residual platinum derived from the cathode was carefully weighed. The analysis of the solution was conducted by precipitation with pure hydrochloric acid exactly as on page 13.

TABLE VI.—ANALYSES OF IGNITED CRYSTALLIZED SILVER.

| Weight Ag + Pt vac. | Weight Pt. | Weight Ag. | Cor. weight fused AgCl vac. | AgCl calc. | Deficiency, mg. |
|------------------------|------------|------------|--------------------------------|------------|--------------------|
| 5.94112 | 0.01833 | 5.92279 | 7.86933 | 7.86938 | 0.05 |
| 5.01726 | 0.01020 | 5.00706 | 6.65256 | 6.65262 | 0.06 |
| | | Total, | 14.52189 | 14.52200 | 0.11 |

¹ THIS JOURNAL, 36, 932 (1914).

² Bur. Standards, *Bull.* 10, 516 (1914). The main quantitative evidence depended upon a single experiment (p. 522), in the interpretation of which the erroneous assumption was tacitly made that inclusion does not exist in the porous cup voltameter, and is the only error in the filter-paper voltameter. The fallacy will be explained more clearly in the next paper upon this topic, to appear shortly.

³ *Proc. Am. Phil. Soc.*, 42, 28 (1903); THIS JOURNAL, 33, 885 (1911).

The conclusion is, therefore, that such finely crystallized electrolyzed silver, which has been ignited at a dull red heat, contains less than 0.001% of impurity. Except for the difficulty of removing the silver from the cathode, and from the clinging contamination of platinum therefrom, this would be a good method of making very pure metal. Possibly the fine crystals precipitated in an electrolytic silver-tree, or by formate, would, on gentle ignition, show equal purity; if so, either of these very obvious processes would be extremely convenient for the preparation of this substance for many quantitative purposes.

In a recent paper Bates and Vinal¹ have compared in a very interesting way the iodine coulometer of Washburn with the silver coulometer. Deviations among the results were noticed, but no satisfactory explanation of them was given. When, however, it is remembered that the investigations made no allowance whatever for included mother liquor, and when one studies the tables on the foregoing pages in this paper, the reasons for the deviations become manifest. With the porous cup voltameter the inclusion is greatest on the largest surface; hence such deposits were the heaviest, as they found. The Kohlrausch form,² because it restricted the surface of the large vessel, would be expected to yield a result between the two; moreover, the error due to anolyte, to be discussed in a subsequent paper, may enter into its results, as well as into those from very diminutive coulometers. The exact correction of these results for inclusions is unfortunately impossible, because the inclusion varies with the extent and roughness of the surface of the cathode. But an approximation may be made if we assume the 120 cc. porous-cup voltameter (which gives the lowest results) as a standard, and then correct its indications by applying the average correction which we have found in this present work (0.015%). This would, of course, raise the calculated atomic weight of iodine by this percentage, if silver is assumed as the standard. Taking silver as 107.88, iodine was found to be 126.898 by Vinal and Bates with the small porous-cup instrument; but corrected for inclusions in the silver this becomes 126.917. This corrected value is in much better agreement with Baxter's best result, 126.932, than before. The remainder of the difference may perhaps be ascribed either to the need of a larger correction for inclusions, or possibly to the existence of a trace of chloride of iodine in the iodine used by Bates and Vinal for standardization. The latter's result is almost identical with Baxter's preliminary value, 126.916.³

The assumed international value of the Faraday is also, of course, affected to an equal extent by inclusion. If, as we cannot but believe,

¹ THIS JOURNAL, 36, 916 (1914).

² Smith's large new form is a modification of the Kohlrausch arrangement.

³ Bates and Vinal took great pains in the purification, but not so much as Baxter. See Baxter, THIS JOURNAL, 32, 1591 (1910); also *Proc. Am. Acad.*, 40, 419 (1904).

the 1.11800 mg. of silver supposed to be deposited by a coulomb contained inclusions, the true value may well be nearer 1.1179. It is profoundly to be regretted that all the able recent experimenters on this absolute value seem to have entirely overlooked the importance of this matter.

We are much indebted to the Carnegie Institution of Washington for apparatus used in this research.

Summary.

In confirmation of earlier work by Lord Rayleigh and that at Harvard, as well as of the subsequent work of Hulett, the presence of included electrolyte in the crystallized silver deposited in a silver coulometer (voltameter) has been shown in the following ways:

First, by quantitative analysis of the crystals after drying to constant weight at 160°.

Secondly, by ignition of the crystals on the cathode at a dull red heat.

Thirdly, by ignition of the crystals, separated from the cathode, in a quartz test tube, arranged so as to prevent evaporation of silver.

Fourthly, by showing that simultaneous deposits which were unequal in weight before ignition had attained equality after ignition.

The included mother liquor was shown by quantitative experiments to be partly within the crystals, and partly between the crystals and the walls of the cathode.

The quantity of the inclusion varies, increasing (as would be expected from the immediately foregoing statement) with increasing surface and with increasing roughness of the cathode. It may vary from 0.004 to 0.035% of the weight of the silver. The silver remaining after the ignition was shown to possess a very high degree of purity, and at incipient redness it was shown to be essentially nonvolatile during brief treatment.

The experiments of the three national bureaus of America, England and Germany, while illuminating in many respects, failed to throw light on the matter, because of incomplete experimentation. Either the temperature of ignition was inadequate, or some other oversight intervened—as, for example, in the attempt to dissolve the precipitated metal in 50 times its weight of mercury when 2500 times its weight are really needed for complete solution.

Because of the variation of the amount of inclusion according to circumstances, it is unfortunately impossible to correct older results. But there seems to be no question that correction is necessary, especially in the case of the large dishes used by Smith, Mather and Lowry. Hence, much of the work should be repeated. The correction affects the value of the electrochemical equivalent, the Faraday, the value assigned to the Standard Weston cell, and all ratios of atomic weights determined electrically; hence, it is a question of importance.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

THE INTERACTION OF HYDROGEN AND CHLORINE UNDER THE INFLUENCE OF ALPHA PARTICLES.

By HUGH STOTT TAYLOR.

Received October 26, 1914.

Recent researches upon the photochemical combination of hydrogen and chlorine have advanced considerably our knowledge of and insight into the reaction itself and to a certain extent the general theory of photochemical reaction. The work of Chapman and his co-workers has, to a great degree, elucidated the abnormalities previously observed and due, in many cases, to the presence of impurities. In the later investigations of the series,¹ by variations from equimolecular mixtures of the two gases, the study of the kinetics of the reaction was commenced. Towards the solution of the latter problem the researches of Bodenstein and Dux² have materially contributed. By the employment of a very ingenious method of measurement, eliminating the necessity of employing water as absorbent for the hydrochloric acid formed, the following points were established:

1. The combination of hydrogen and chlorine in light is a reaction of the second order, the velocity being proportional to the square of the chlorine concentration. Hydrogen is without influence so long as it is present to the extent of at least $\frac{1}{4}$ of the amount of chlorine. At smaller hydrogen concentrations the velocity decreases slightly.

2. The hydrochloric acid formed is without influence on the velocity.

3. Water vapor within certain limits (0.004–2.3 mm.) is also without influence.

4. Oxygen retards the reaction, such that the velocity at all stages of the decomposition is inversely proportional to the oxygen concentration.

For the interpretation of the equation of reaction thus obtained:

$$+ \frac{d(2\text{HCl})}{dt} = k \frac{J_0 [\text{Cl}_2]^2}{[\text{O}_2]}$$

Bodenstein³ has developed a theory of photochemical reaction velocities and applied it to practically all the measurements in this branch to be found in the literature. According to this theory the initial absorption process in any photochemical change is to be regarded as a photoelectric effect, as a rupture of the molecule at the expense of the absorbed light energy into a positive radical—an atom or with more complex substances a molecule with a free valence—and a free electron. Both portions may lead to chemical reaction, the positive radicals in that they are, chem-

¹ Chapman and Underhill, *J. Chem. Soc.*, 103, 496 (1913).

² *Z. physik. Chem.*, 85, 297 (1913).

³ *Ibid.*, 85, 330 (1913).

ically, exceedingly active, the electrons in that they may attach themselves to molecules and so activate them as to take part in chemical change. A distinction is drawn between primary light reactions, in which the positive radicals enter into combination, and secondary reactions in which the molecules activated by the electrons take part in the reaction, the electrons, after reaction has occurred, being again free to attach themselves to and activate other molecules.

A further development of the theory, as regards the relation of light energy absorbed to chemical reaction produced, reveals a marked point of difference in regard to the two classes of reaction. In the primary reactions, for every molecule brought into combination a quantum of absorbed energy or a small number of quanta is regarded as necessary. In the secondary reactions, owing to the function of the free electron as catalyst, an energy quantum should be in a position to bring about the combination of a large number of the reacting molecules.

If it be true that the first stage of a photochemical reaction, as assumed in the theory of Bodenstein, consists of a photoelectric effect, the rupture of a molecule into a positive radical and an electron, then the theory and the method of development should find rigid application in all such chemical reactions as are effected under the influence of other forms of energy, provided that under such influence the rupture of the molecule with the formation of free electrons may be postulated. It is obvious, therefore, that such processes as are effected by means of electrical energy in gases (*e. g.*, under the influence of the silent electric discharge or of Röntgen rays) or, on the other hand, processes determined by radioactive forms of energy should show a parallelism to those in which light is employed as the source of energy.

As regards reactions brought about by means of the silent discharge or by Röntgen rays, the literature does not reveal a large number of examples. The formation of ozone as studied by Krüger,¹ and the decomposition of ammonia investigated by Davies,² show points of resemblance to the primary light reactions. Quite recently an investigation by Le Blanc and Volmer³ on the combination of hydrogen and chlorine under the influence of Röntgen rays shows, as regards the ratio of energy supplied to chemical reaction produced, a parallelism to the secondary light reactions. Concerning this particular research a more detailed discussion will be given later.

The literature of reactions assisted by radioactive forms of energy has been admirably collected and discussed in detail by Lind.⁴ The author

¹ Nernst, *Festschrift*, Halle, p. 240 (1912).

² *Z. physik. Chem.*, **64**, 657 (1908).

³ *Z. Elektrochem.*, **20**, 494 (1914).

⁴ *J. Phys. Chem.*, **16**, 564 (1912).

came to the conclusion that in reactions caused by alpha particles, as many molecules are brought into reaction as ions are formed in the same period of time. From a careful study of the ozonization of oxygen under the influence of alpha particles, Lind formulated an "Ionic theory of ozonization," comparable in every way with the theory of primary light reactions as developed by Bodenstein. The theory was shown to be applicable, with one exception, to the reactions caused by radioactive energy then studied. The exception to the above formulation of Lind was the combination of hydrogen and chlorine. Jorissen and Ringer¹ studied this reaction, using a radium salt as the source of energy, the measurements being made in an actinometer over water. According to the calculations of Lind, for every ion produced by the radiant energy 100 to 1000 molecules of hydrogen chloride result. It was further shown that, in this case also, as regards a period of induction and irregularity of sensitivity of the gaseous mixture, due doubtless to variation of its oxygen content, the reaction ran parallel to the photochemical change.

It appeared, therefore, probable that the combination of hydrogen and chlorine under the influence of energy from radioactive sources would prove an interesting and valuable subject for closer investigation. Owing to the development of experimental technique in late years it should be possible not only to evaluate the energy relationships of the reaction but to elucidate the kinetics of the combination.

Experimental.

The method employed in the present work is, with suitable modifications, that employed by Lind² in the study of the ozonization of oxygen.

The reaction vessel consisted of a large bulb 12 cm. in diameter into the base of which was sealed the vessel designed to hold the emanation. This consisted of a tube drawn out to a fine thin-walled capillary on the end of which was blown a small bulb approximately 1 cu. mm. vol., uniform as regards thickness of wall. The preparation of such bulbs has been very fully described by Lind³ and the same procedure was adopted in the present instance with one modification. To create the requisite pressure inside the tube during the drawing of the capillary and the blowing of the bulb, a bomb of compressed nitrogen was employed instead of the foot bellows. In this way a more uniform and more easily regulated pressure was obtained. Each bulb was tested as to strength, uniformity and range. They were tested to withstand a vacuum and an excess pressure of one atmosphere. The uniformity and range were determined by filling the bulb with radium emanation followed by measurement of the diameter of the luminescent circle produced on a zinc sulfide screen placed

¹ *Ber.*, 39, 2095 (1906).

² Wiener, *Monatshefte*, 32, 295 (1912).

³ *Loc. cit.*

at measured distances from the bulb and on all sides of it. An interval of from two to three hours intervened between the filling of the bulb and the making of the measurements, during which time the emanation comes into equilibrium with its disintegration products, in particular with Radium C, with alpha particle range 7.06 cm. in air. Finally a bulb was chosen of uniform range, averaging 5.6 cm. The determination was not effected without difficulty, as the quantity of radium available (10 mg.) was very small for securing sufficient illumination of the zinc sulfide screen.

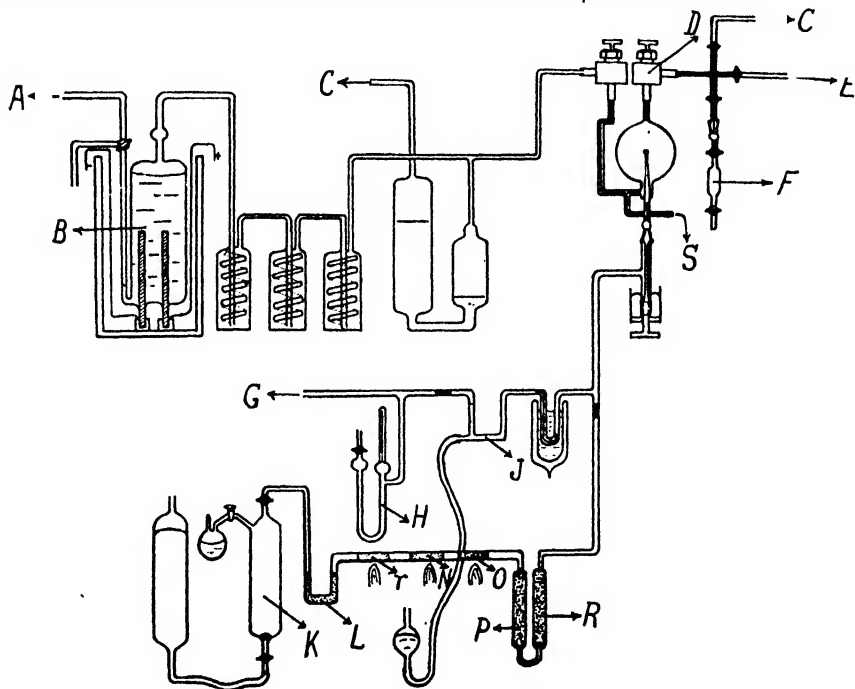


Fig. 1.

- | | | |
|-------------------------------|-------------------------------------|--------------------------|
| A. HCl inlet. | G. To Gaede pump. | r. Lead dichromate. |
| B. Gas generator. | H. MacLeod gage. | N. Copper. |
| C. Outlet to absorber. | J. Mercury trap. | O. Copper oxide. |
| D. Platinum tap. | K. Vessel for collecting emanation. | P. Solid caustic potash. |
| E. To water and Töpler pumps. | L. Anhydrous calcium chloride. | R. Phosphorus pentoxide. |
| F. Sampling vessel. | | S. To manometer. |

The hydrogen and chlorine were generated in stoichiometric proportions by the electrolysis of concentrated hydrochloric acid. A vessel of 6 l. capacity was employed, the electrodes consisting of Acheson graphite rods 1 cm. in diameter, soaked in hot paraffin wax in a vacuum. These electrodes were sealed into the glass vessel with marine glue over which a thick layer of paraffin wax was poured. Through a side tube, hydrogen

chloride could be led in from time to time, whereby the exhausted hydrochloric acid could be again concentrated. The gases passed from the generator through three spiral wash-bottles, one filled with water followed by two containing concentrated sulfuric acid. They were then conducted to a gasometer in which they could be stored over concentrated sulfuric acid and from which they could be directed either to the reaction vessel or to an absorber.

The entrance to, and exit of the gases from, the reaction vessel were controlled by two platinum taps such as were employed by Bodenstein and Dux¹ in their photochemical investigations. By this means the use of tap-grease and consequent contamination of the gases with organic matter was avoided. The pressure in the reaction vessel was measured by means of the Bodenstein quartz-glass manometer attached by a quartz-in-glass ground joint to a capillary side-tube sealed into the capillary entrance tube of the vessel. The gases were led in from below and conducted out from above to the second platinum tap by means of capillary glass tubing. In this way the volume of dead space, outside the reaction-bulb itself, was reduced to a minimum.

During the reaction the gases were kept mixed by a small circular electric heater placed about 5 cm. from the base of the bulb, and against it. This ensured a slight local heating, causing an upward motion of the gases. Around the top of the bulb was placed a brass collar into which ice could be put in order to cool the gases, to bring about the downward motion. The device worked quite efficiently and caused no difficulties due to temperature variations, as was demonstrated by the perfect constancy of the pressure in the bulb over the extended periods of time intervening between successive measurements of the reaction velocity.

After leaving the reaction vessel the gases could pass by means of a four-way capillary tube in either of two directions. During the process of cleaning the apparatus by washing out with the electrolytic gases, they could be directed to an absorber. During the experiment samples could be taken in an evacuated receiver, which could be evacuated first by means of a water-pump and finally by means of a Töpler pump. The receiver was attached to the four-way capillary tube with the aid of a ground glass joint and by a suitable arrangement of glass taps the various operations could be performed. During purification the taps to the pump and the receiver were closed. During evacuation of the receiver the platinum tap and that to the absorber were closed, while as the sample was being taken the taps to the absorber and pump were closed. By momentarily opening the platinum tap to the evacuated receivers, which were about 25 cc. capacity, a sample of gas sufficient for analysis could be obtained. After each successive withdrawal of gas the pressure in the reaction vessel

¹ *Loc. cit.*

was noted. The gases were analyzed after absorption in potassium iodide solution by titration of the liberated iodine with standard thiosulfate solution and estimation of the hydrochloric acid—after expulsion of dissolved carbon dioxide by boiling—with standard baryta solution.

The emanation was obtained from 10 mg. of radium bromide. It was collected from the slightly acidified aqueous solution of the salt in an apparatus similar in every way to that described by Lind, which calls, therefore, for no further description here.

The method of purification employed was a modified form of the procedure adopted in the laboratory of Mme. Curie and described by Lind. The emanation passed from the cylinder in which it was collected, first over heated lead dichromate, copper and copper oxide, to decompose any organic impurities and to remove hydrogen and oxygen. Thence it passed over caustic potash and phosphorus pentoxide through a T-piece into a tube connecting a U-tube with the capillary and bulb sealed into the reaction vessel. The U-tube contained a length of copper wire upon which the emanation could be condensed when the tube was cooled in liquid air. Beyond the U-tube came a mercury trap followed by a MacLeod gage and Gaede mercury pump.

After evacuation of the purification apparatus, capillary and bulb to 0.0001 mm., the mercury trap was closed and the emanation allowed to pass into the purification tubes and to circulate over the heated portions and absorbents into the remaining tubes. After one to two hours the residual gas was collected in the U-tube by cooling this in liquid air, the mercury trap opened and the uncondensed gases remaining were pumped away. The glass was then sealed at the T-piece and still further evacuated to 0.0001 mm. This completed, the mercury trap was again closed and the tube between it and the MacLeod gage was sealed. By withdrawal of the liquid air and by slight warming of the U-tube, the emanation was vaporized. It was then pumped, by means of the mercury in the mercury trap, into the small emanation bulb.

Special attention is directed to Fig. 2, illustrating the arrangement of the emanation bulb. In the study of the ozonization of oxygen it was found by Lind that an uncontrollable variation of the ozone formation, for unknown reasons, could not be avoided. Such variations in the present series of measurements would render a study of the kinetics of the reaction impossible, as a reaction constant must be derived to distinguish the order of reaction. A careful examination of the experimental technique employed by Lind suggested one possible source of error, the variation of the level of mercury, at the neck of the emanation bulb due to variations in the temperature of the apparatus or of the barometric pressure. These could quite possibly be considerable, as the period of experiment varied from 12 to 24 hours. They could operate in two directions. Either

the mercury could rise into the bulb, in which case some of the alpha particles would be absorbed by the mercury and the lower portion of the apparatus being shielded by the mercury, ozonization would not occur

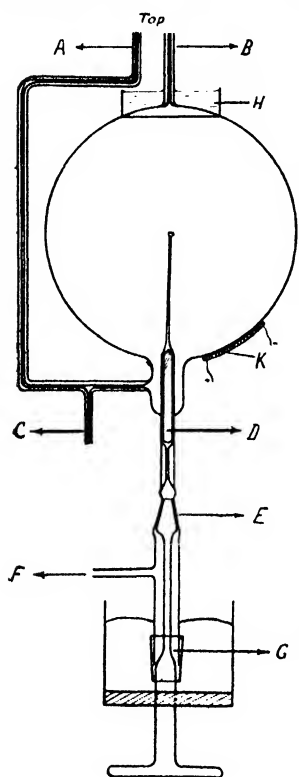


Fig. 2.

- A. Capillary inlet from platinum tap.
- B. Capillary outlet to platinum tap.
- C. Capillary connection to manometer.
- D. Silica compensator rod.
- E. Ground glass joint.
- F. Inlet for emanation.
- G. Rubber connection.
- H. Ice reservoir.
- K. Electric heater.

there; or, on the other hand, the mercury level might fall in the capillary, withdrawing the emanation partially from the bulb into the tube through the wall of which the alpha particles could not penetrate. It is difficult to imagine that these variations could alone be responsible for the considerable variations of the experimental results, but in the present series of measurements a device was employed whereby this possible source of error was eliminated.

Immediately below the seal of the capillary in the reaction vessel a ground glass joint was attached, fitted with a tight fitting plunger which operated through a rubber band in the base of the wider tube to which the joint was sealed. The rubber band was sealed both to the wider tube and the plunger by means of marine glue and was rendered vacuum-tight by surrounding it with an outer vessel containing mercury. The emanation entered the wider tube from the purification apparatus through a tube sealed into the side. By pushing the plunger home and suitably supporting it, a mercury-tight seal could be made at the ground glass joint, while by stretching the rubber connection the joint could be opened. In actual work the mercury was brought to such a level in the capillary emanation tube that on pushing the plunger home the mercury rose just to the neck of the bulb.

In this manner influences of barometric pressure were eliminated. It is obvious, however, that with the tube closed at the ground glass joint the bulb and the mercury above the seal would functionate as a thermometer

and that changes in temperature would affect the level of mercury in the capillary. To obviate this difficulty an interesting device was employed. By inserting a piece of fused silica (whose coefficient of expansion is very low) in the open space above the ground glass joint, the greater expansi-

bility of the mercury over that of the glass was corrected for. A knowledge of the rates of expansion of the three substances and of the volume occupied by the mercury in the absence of the silica enabled one to calculate the volume of silica required. In this way variations in the level of the mercury due to temperature changes were obviated and a constant level obtained. The device functioned admirably. On one occasion where for experimental reasons (see p. 20) the mercury was cooled twenty to thirty degrees, the level in the tube showed only minute variation.

Theoretical.

The processes occurring may be set forth as follows:¹

1. In the passage of an alpha particle through the gaseous mixture, ionization is produced and the chlorine molecules decompose into positively charged radicals and electrons.

2. The electrons disappear in two ways:

(a) They add on to oxygen molecules, activate these, yielding probably ozone which again forms oxygen (the function of oxygen in the photochemical reaction has been elaborately set forth by Bodenstein and in the present deductions the assumptions then made have been followed).

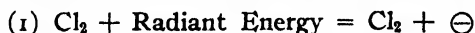
(b) They attach themselves to chlorine molecules, yielding the negatively charged chlorine molecules which are the material for the formation of hydrogen chloride.

3. The negatively charged chlorine molecules disappear in two ways:

(a) They regenerate neutral chlorine molecules in that their electrons neutralize themselves with the positively charged rests formed in (1), or in some other way lose their charge.

(b) They react with hydrogen to form hydrogen chloride with regeneration of the electron, which then enters upon the cyclic process again and continues thus until eliminated as postulated by (2a).

The equations representing these processes may be represented thus:



The corresponding reaction velocity equations are:

$$(1) \quad + \frac{d\ominus}{dt} = k_1 J \text{ absorbed.}$$

In the experimental conditions chosen, all the alpha particles are absorbed and so

$$+ \frac{d\ominus}{dt} = k_2 J \quad (A)$$

¹ Cf. Bodenstein, *Loc. cit.*, p. 346, *et seq.*

where J is the radiant energy employed.

$$(2a \text{ and } b) - \frac{d\ominus}{dt} = k_4[\ominus][O_2] + k_5[\ominus][Cl_2].$$

On attainment of equilibrium conditions,

$$+ \frac{d\ominus}{dt} = - \frac{d\ominus}{dt}$$

$+ \frac{d\ominus}{dt}$ is composite, being determined by reaction Equation A and the process of regeneration of electrons detailed in (3b). This latter is identical with, and is, therefore, equal to,

$$k_8 [Cl_2^-] [H_2].$$

Assuming that each Cl_2^- formed combined instantaneously with H_2 we have

$$+ \frac{d[2HCl]}{dt} = + \frac{d[Cl_2^-]}{dt} = k_5[\ominus] [Cl_2] \quad (B)$$

Therefore

$$+ \frac{d\ominus}{dt} = k_2 J + k_5[\ominus] [Cl_2]$$

and so

$$k_2 J + k_5[\ominus] [Cl_2] = k_4[\ominus] [O_2] + k_5[\ominus] [Cl_2]$$

Whence

$$[\ominus] = \frac{k_2 J}{k_4[O_2]}.$$

From (B), therefore, we get

$$+ \frac{d[Cl_2^-]}{dt} = \frac{d[2HCl]}{dt} = k_2 \frac{k_5}{k_4} \cdot \frac{J[Cl_2]}{[O_2]}$$

a reaction velocity equation of the first order, derived with the assumption that the formation of hydrogen chloride results from the combination of negatively charged molecules of chlorine with hydrogen molecules and that this combination is instantaneous. Were this not the case, a consideration of the reaction equations will show that, if both hydrogen and chlorine were involved in the electronic processes, the formation of hydrogen chloride would yield a velocity equation of the second order.

The experimental results presented below offer a justification for the viewpoint adopted. Column 1 gives the times, in hours, at which measurements were made. In the second column are recorded the pressures. Columns 3 and 4 give the titers of chlorine and hydrochloric acid, respectively. To ensure greater accuracy, the acid titer was made with a more dilute solution (normality of baryta solution, one-third the normality of the thiosulfate solution) than was employed for the titration of the iodine, but in the tables they are presented in equivalent units. Column 5 gives the total volume of hydrogen, chlorine and hydrogen chloride in the same

units, whence the actual volumes in millimeters of mercury presented in Columns 6 and 7 could be calculated. Columns 8 and 9 give $d[2\text{HCl}]$ and dt , respectively, while Column 10 gives the reaction constant k_a calculated from point to point for the simple differential equation

$$+ \frac{d[2\text{HCl}]}{dt} = k_a [\text{Cl}_2].$$

Column 11 gives the correction-factor E for the decay of emanation calculated from the equation

$$\text{Log } E = \frac{\text{Log } E \text{ at time } t + \text{Log } E \text{ at time } t + dt}{2}$$

assuming the initial factor for E to be 100. Column 12 gives the values (k_b) after the introduction of this correction in (k_a). Hence the differential equation employed in this column may be written thus:

$$+ \frac{d[2\text{HCl}]}{dt} = k_b E [\text{Cl}_2]$$

Column 13 gives the value (k_c) of (k_b) multiplied by the pressure during the given time interval. The reason for this is obvious. Since samples are constantly withdrawn for analysis it is obvious that the oxygen concentration also undergoes constant diminution in amount proportional to the volume of gas withdrawn. The equation is, therefore:

$$+ \frac{d[2\text{HCl}]}{dt} = k_c E \frac{[\text{Cl}_2]}{\text{Total Pressure, } P}$$

whence it follows that:

$$\frac{k_c}{P} = k_2 \frac{k_5}{k_4} \cdot \frac{1}{[\text{O}_2]}$$

as derived in the theoretical portion of this paper.

The hydrogen and chlorine were passed into the evacuated reaction vessel from the gasometer two to three hours after the bulb was filled with emanation. The gases were analyzed immediately in all except the first experiment, Table I, in which case the first analysis ($t = 0$) was made one hour after filling. The experiments were carried out, naturally, in a dark room illuminated by the light of a single carbon filament lamp enclosed in a yellow covering. The reaction vessel was further protected against illumination by a covering of thick black paper.

The results of the four experiments are given in Tables I to IV.

It is evident that in the initial stages of the reaction a period of induction was present. This was doubtless due to impurities in the reaction vessel caused by a modification of the apparatus a day or two previous to the commencement of the experiments. The time available for the completion of the work did not permit of an elimination of this by extended cleansing of the apparatus with the electrolytic gases. Conse-

quently, the induction period was also found in the two following series. In the fourth series this influence seems to have disappeared.

TABLE I.

| t. | P. | Titer. | | $H_2 + Cl_2 + 2HCl.$ | Mean value | | $dHCl.$ | dt. | $k_a.$ | Emanation correction. | $k_b.$ | $k_c.$ |
|-------|-------|---------|------|----------------------|----------------|----------------------|---------|-------|--------|-----------------------|--------|--------|
| | | $Cl_2.$ | HCl. | | Mm. HCl. | Mm. H_2 or $Cl_2.$ | | | | | | |
| 0 | 676.5 | 18.35 | 0.50 | 37.20 | 9.15 13.45 | 332.6 | 4.30 | 1 | 12.93 | 99.0 | 13.06 | 8.83 |
| 1 | 657.5 | 16.27 | 0.66 | 33.20 | 13.07 26.02 | 319.0 | 12.95 | 1.75 | 23.20 | 98.0 | 23.68 | 15.56 |
| 2.75 | 638.7 | 16.50 | 1.36 | 34.36 | 25.28 47.15 | 301.2 | 21.87 | 3.91 | 18.57 | 96.0 | 19.34 | 12.36 |
| 6.66 | 620.7 | 13.80 | 2.20 | 29.80 | 45.82 72.65 | 280.7 | 26.83 | 5.0 | 19.12 | 92.8 | 20.60 | 12.79 |
| 11.66 | 602.8 | 12.45 | 3.30 | 28.20 | 70.55 140.6 | 248.6 | 70.05 | 13.14 | 21.44 | 86.6 | 24.76 | 14.92 |
| 24.8 | 585.2 | 9.30 | 5.66 | 24.26 | 136.6 163.7 | 217.5 | 27.10 | 6.7 | 18.60 | 80.3 | 23.17 | 13.56 |
| 31.5 | 569.7 | 8.85 | 6.87 | 24.57 | 159.3 211.9 | 192.0 | 52.60 | 16.4 | 16.71 | 73.6 | 22.70 | 12.93 |
| 47.9 | 551.8 | 6.90 | 8.17 | 21.97 | | | | | | | | |

A rough test of the reactivity of the gases towards light showed that, although reactive, they were by no means comparable in activity with the gases employed by Bodenstein and Dux. The cause for this lay doubtlessly in the exhaustion of the hydrochloric acid from which the gases were produced.

TABLE II.

| t. | P. | Titer. | | $H_2 + Cl_2 + 2HCl.$ | Mean value | | $dHCl.$ | dt. | $k_a.$ | Emanation correction. | $k_b.$ | $k_c.$ |
|-------|-------|--------------|----------------|----------------------|----------------|----------------------|---------|------|---------|-----------------------|---------|---------|
| | | $Cl_2.$ | HCl. | | Mm. HCl. | Mm. H_2 or $Cl_2.$ | | | | | | |
| 0 | 698.5 | 16.65 | 0.566 | 33.87 | 11.68 13.43 | 343.0 | 1.75 | 1 | 5.10 | 99.7 | 5.12 | 3.58 |
| 1 | 678.7 | 18.00 | 0.706 | 36.71 | 13.05 21.24 | 330.3 | 8.19 | 1 | 24.08 | 99.0 | 24.32 | 16.51 |
| 2 | 660.0 | 15.63 | 1.01 | 32.37 | 20.65 39.01 | 315.1 | 18.36 | 2 | 29.14 | 98.0 | 29.73 | 19.62 |
| 4 | 640.7 | 15.70 | 1.973 | 33.37 | 37.84 56.50 | 296.7 | 18.66 | 2 | 31.45 | 96.4 | 32.62 | 20.90 |
| 6 | 622.7 | 13.10 | 2.533 | 28.73 | 54.90 66.59 | 281.0 | 11.69 | 2 | (20.80) | 95.0 | (21.90) | (13.64) |
| 8 | 577.2 | 12.80 | 3.066 | 28.67 | 61.73 127.5 | 241.3 | 65.77 | 9.2 | 28.97 | 91.0 | 31.84 | 18.38 |
| 17.2 | 526.1 | 9.00 | 5.10 | 23.10 | 116.2 138.1 | 199.5 | 21.90 | 3.55 | 30.91 | 86.7 | 35.66 | 18.76 |
| 20.75 | 435.9 | 8.13 5.70 | 5.783 4.866 | 22.04 16.27 | 114.4 130.4 | 156.7 | 16.00 | 3.25 | 31.42 | 84.5 | 37.20 | 16.20 |

The last value in Table III is of interest in view of the remarks made previously as to the importance of maintaining the mercury at a constant level in the emanation bulb tube. The sudden fall in the constant k_c

of the last measurement could not be accounted for until an observation of the reaction vessel showed that from some unknown cause (probably a release at the ground glass joint) the mercury level had fallen a centimeter or so in the capillary withdrawing, therefore, some of the emanation from the bulb, and so decreasing the energy factor E in the equation.

TABLE III.

| t. | P. | Titer. | | $H_2 + Cl_2 + 2HCl.$ | Mean value H_2 or Cl_2 . | | $dHCl.$ | dt. | $k_a.$ | Emanation correction. | $k_b.$ | $k_c.$ |
|---------------|-------|--------------|---------------|----------------------|------------------------------|-------------|---------|---------|--------|-----------------------|--------|--------|
| | | $Cl_2.$ | HCl. | | Mm. HCl. | Mm. | | | | | | |
| 0 | 697.5 | 19.15 | 0.466 | 38.77 | 8.38 15.94 | 342.7 | 7.56 | 2.1 | 10.50 | 99.3 | 10.57 | 7.37 |
| 2.1 | 678.8 | 17.10 | 0.80 | 35.00 | 15.51 27.74 | 328.6 | 12.23 | 1.9 | 19.59 | 98.0 | 19.98 | 13.57 |
| 4 | 658.6 | 17.20 | 1.466 | 35.87 | 26.92 36.94 | 313.3 | 10.02 | 2 | 16.00 | 96.4 | 16.60 | 10.93 |
| 6 | 640.2 | 13.60 | 1.517 | 28.82 | 35.91 91.94 | 288.1 | 56.03 | 10.1 | 19.26 | 92.2 | 20.89 | 13.37 |
| 16.1 | 620.2 | 13.12 | 4.40 | 30.64 | 89.06 105.8 | 261.4 | 16.74 | 3.9 | 16.42 | 87.4 | 18.79 | 11.65 |
| 20 | 602.8 | 12.20 | 5.017 | 29.42 | 102.8 122.3 | 245.1 | 19.50 | 4.1 | 19.40 | 84.5 | 22.95 | 13.83 |
| 25.1 | 303.2 | 11.10 | 5.65 | 27.85 | 61.5 112.7 | 108.0 | 51.20 | 18.4 | 25.77 | 77.3 | 33.34 | 10.11 |
| 43.5 67.75 | 294.4 | 3.80 2.80 | 4.50 5.266 | 12.10 10.87 | 109.5 142.6 | 84.0 (33.1) | 24.25 | (16.25) | 65.9 | (24.65) | (7.36) | |

TABLE IV.

| t. | P. | Titer. | | $H_2 + Cl_2 + 2HCl.$ | Mean value H_2 or Cl_2 . | | $dHCl.$ | dt. | $k_a.$ | Emanation correction. | $k_b.$ | $k_c.$ |
|--------------|----------------|--------------|---------------|----------------------|------------------------------|-------|---------|------|--------|-----------------------|--------|--------|
| | | $Cl_2.$ | HCl. | | Mm. HCl. | Mm. | | | | | | |
| 0 | 858.0 | 15.76 | 7.66 | 39.18 | 167.7 181.1 | 341.8 | 13.4 | 1 | 39.2 | 99.7 | 39.32 | 33.7 |
| 1 | 835.2 | 13.12 | 7.02 | 33.26 | 176.3 183.6 | 327.6 | 7.3 | 1 | 22.3 | 99.0 | 22.53 | 18.8 |
| 2 | 807.2 | 14.18 | 7.99 | 36.35 | 177.4 185.1 | 313.0 | 7.7 | 1 | 24.6 | 98.3 | 25.04 | 20.2 |
| 3 | 756.0 | 10.98 | 6.533 | 28.49 | 173.4 189.0 | 287.4 | 15.6 | 2 | 27.1 | 97.2 | 27.92 | 21.1 |
| 5 | 733.2 | 12.00 | 8.00 | 32.00 | 183.3 196.1 | 271.7 | 12.8 | 2 | 23.56 | 95.7 | 24.62 | 18.0 |
| 7 | 671.3 | 10.30 | 7.523 | 28.12 | 179.6 240.6 | 230.6 | 61.0 | 10 | 26.45 | 91.5 | 28.90 | 19.4 |
| 17 | 652.7 | 7.20 | 8.04 | 22.44 | 233.9 243.5 | 207.0 | 9.6 | 2 | 23.19 | 87.3 | 26.56 | 17.3 |
| 19 | 601.5 | 7.27 | 8.656 | 23.20 | 224.0 235.5 | 185.9 | 11.5 | 2.6 | 23.79 | 85.7 | 27.75 | 16.7 |
| 21.6 | 585.4 | 5.96 | 7.693 | 19.61 | 229.6 246.7 | 173.6 | 17.1 | 3.1 | 31.77 | 84.0 | 37.83 | 22.1 |
| 24.7 | 544.3 | 5.72 | 8.333 | 19.77 | 229.4 291.6 | 141.9 | 62.2 | 16.8 | 26.10 | 78.0 | 33.40 | 18.2 |
| 41.5 46.2 | 528.0 510.0 | 4.33 3.86 | 9.99 10.07 | 18.65 17.79 | 282.8 298.8 | 118.6 | 16.0 | 4.7 | 28.70 | 71.9 | 39.92 | 21.1 |

At such low pressures as are reached in the later measurements of Expt. 3 (pressures 303 and 294 mm.) it is obvious that the absorption of the alpha particles cannot be regarded as complete, and the value found for k_c is low. To avoid a correction for incomplete absorption and yet at the same time obtain an extended range of pressure variation, Expt. 4 was performed. The residual gases from Expt. 3 were left in the reaction vessel, which was then cooled in a mixture of solid carbon dioxide and acetone. Fresh hydrogen and chlorine were led into the vessel from the gasometer until it was full at the prevailing temperature. The taps were then closed and the cooling mixture removed. On the attainment of room temperature it is clear that the reaction vessel was filled with a hydrogen, chlorine, hydrochloric acid mixture at more than atmospheric pressure. It was during this operation that the contrivance for maintaining a constant mercury level in the capillary emanation tube was shown to functionate so well; for at the low temperature attained (about -20° , as calculated from the pressure measurement) the contraction in volume of the mercury was quite small.

Discussion of the Results.

The constancy of the values tabulated in the last column, k_c , of the several tables permits of the following conclusions being drawn:

1. The combination of hydrogen and chlorine under the influence of alpha particles is a reaction of the first order. As the hydrogen and chlorine are present in equivalent amounts it is not possible to state definitely from the results that the reaction is proportional to the chlorine concentration, though this is probably the case. This point could only be established by variation of the ratios of hydrogen to chlorine employed.
2. The hydrochloric acid formed is without influence on the velocity.
3. Oxygen retards the reaction, such that the velocity at all stages of the decomposition is inversely proportional to the oxygen concentration.
4. The experimental facts may be interpreted by means of a reaction velocity equation:

$$+ \frac{d[2\text{HCl}]}{dt} = k J \frac{[\text{Cl}_2]}{[\text{O}_2]}$$

It will, therefore, be seen that, as regards the kinetics of the combination, the reaction shows complete parallelism to the photochemical reaction. The point of divergence in the two velocity equations, *viz.*, the power of the chlorine concentration, is readily explainable by the fact that in the one case absorption of the available energy is complete and in the other quite small.

As regards parallelism between the ratios of energy absorbed to reaction produced, unfortunately, little can be said from the present work. The condition of affairs prevailing in Central Europe prevented a con-

tinuance of the work in the direction of more reactive gases and determination of the amount of radioactive energy employed. In this connection, however, the calculations of Lind from the results of Jorissen and Ringer tend to show that for each ion produced by the radiant energy 100 to 1000 molecules of hydrogen chloride are formed. Also, it must be remembered that the amount of oxygen present in the gaseous mixture exercises a profound influence on the energy ratio, as the present results and those of Chapman and Bodenstein show. For, it follows as a natural consequence of the reaction velocity equation developed, that in gases of absolute purity the reaction would be infinitely rapid; that is, a small quantity of energy would suffice to bring about an infinitely large combination of the gases. This conclusion is confirmed in the observation that extremely pure gases tend so easily to explode.

The point should be especially borne in mind when drawing conclusions such as were recently drawn by Le Blanc and Volmer.¹ The energy ratio required in the light reaction according to the calculations of these authors, *viz.*, that one electron must catalyze at least 10^{12} molecules, would easily be realized in an explosive mixture of the gases. Also, with regard to the further suggested proof which the authors bring forward—namely, that Röntgen rays bring about combination, but that in their gas mixture, at the most 10^4 molecules combine as a result of the liberation of one electron or ion—it must be recognized that such proof cannot be regarded as sound if, as seems very probable from analogy with the present communication, oxygen retards the rate of reaction. The authors mention further that their experimental conclusions do not exclude the possibility of the hydrogen-chlorine combination taking place through a loosening (*Lockerung*) of the electrons such as was postulated by Stark. This observation overlooks one consequence of the theory of Stark, already emphasized by Bodenstein,² “*der Fall, dass mehr als eine Molekel durch ein Quantum umgesetzt werden kann, ist bei Starks Darlegungen überhaupt nicht vorgesehen.*” As their results show, 10^4 molecules combine due to one ion.

It is evident, therefore, that an extension of this field of work with a view to determining the kinetics of the hydrogen-chlorine combination under the influence of Röntgen rays would not fail to be of interest. Also, an exact evaluation of the energy employed to chemical reaction produced, with a gas of *constant* composition, under the three influences, light, radioactive energy, and Röntgen rays, should be invaluable for the gaining of a closer insight into the reaction mechanism.

Summary.

The kinetics of the combination of hydrogen and chlorine under the influence of the alpha particles from radium emanation has been studied.

¹ *Loc. cit.*

² *Ibid.*, p. 394.

The technique of such radioactive investigations has been improved with a view to giving greater constancy of experimental conditions.

The reaction has been shown to be one of the first order, in agreement with a theory developed, whereby the velocity of formation of hydrochloric acid should be proportional to the energy employed and to the chlorine concentration, inversely proportional to the oxygen concentration.

The analogy between the photochemical reaction and the reaction studied has been emphasized and the bearing of the experimental results on the problem of the photochemical and Röntgen ray reactions has been discussed.

The experimental work of the preceding paper was carried out in the Koenigliche Technische Hochschule zu Hannover. To Professor Max Bodenstein, at whose suggestion the research was undertaken, the author wishes to express his deep indebtedness, as well for the generous advice and kindly interest as for the many details of experimental technique which made the work possible.

PRINCETON, N. J.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY,
No. 242.]

THE DENSITIES AND DEGREES OF DISSOCIATION OF THE SATURATED VAPORS OF THE AMMONIUM HALIDES, AND THE RELATED THERMAL DATA.

BY ALEXANDER SMITH AND ROBERT H. LOMBARD.

Received November 13, 1914.

In the case of solids undergoing thermal dissociation the data which possess the greatest chemical significance are those relating to the *saturated* vapors, in which the components of the vapor are in equilibrium with each other and with the solid. Yet, in regard to the great majority of even the most familiar of such substances, as, for example, phosphorus pentachloride and the ammonium halides, definite, quantitative information in this direction has been absolutely lacking. The vapor (dissociation) pressures have been determined, sometimes repeatedly, but for the most part the densities of the unsaturated vapors (namely, at atmospheric pressure) have alone been measured. Of the very few systems involving saturated vapors which have been subjected to exact study, those of the sulfides of ammonium (Isambert and others) and calomel (Smith and Menzies¹) may be mentioned.

As regards the ammonium halides, their dissociation pressures had not been determined with the requisite degree of accuracy. To secure consistent values for use in the present investigation, these pressures have

¹ THIS JOURNAL, 32, 1541 (1910); *Z. physik. Chem.*, 76, 251.

been redetermined by Smith and Calvert,¹ using a thermometer identical with that employed in the present work, a bath similarly jacketed but smaller, and the same samples of the ammonium halides.

As regards the vapor densities of the ammonium halides, it is commonly assumed by chemists that the dissociation is complete, and that the densities correspond with this assumption. Only the comparatively easily measured densities of the *unsaturated* vapors have been determined, however, and the results of the present work show that this assumption is very far from being correct. In the present research the densities of the saturated vapors of the ammonium halides have been investigated. The results, together with the corresponding dissociation pressures of Smith and Calvert, have made it possible now to ascertain by calculation, and to give for these substances the values of the degrees of dissociation, the dissociation constants, the partial pressures of the dissociation products, the heats of dissociation, and the latent heats of vaporization.

Previous Determinations of the Vapor Densities.—In Table I the results of previous determinations are given. The methods used (Col. 2) are indicated thus: D. (Dumas), H. (Hofmann), V. M. (V. Meyer). The temperature (Col. 3) is the value assumed by the observer. The heating was effected by the vapor of the substance indicated in Col. 4, boiling (save in one instance) under the existing atmospheric pressure. The actual temperatures obtainable with the vapors of these substances vary considerably with the existing atmospheric pressure, yet Ramsay and Young are the only observers who corrected the boiling point of the bath liquid on this account. The actual temperatures obtainable vary still more (5° to 8° or more) according as much, little, or no jacketing is used. None of the observers mention jacketing and presumably they used none. The recorded temperatures must therefore be, for the most part, considerably higher than those actually attained.

For the purpose of comparison, the observed vapor densities (Col. 5), originally given on such scales as air = 1, hydrogen = 1, or mols per liter, have all been re-calculated to weights of 1 cc. at 0° and 760 mm. The calculated values for the density, assuming no dissociation (δ) are given for each substance after its name. The per cent. dissociated (Col. 6) has been calculated from the values of δ , and of Δ (Col. 5).

Discussion of Previous Determinations.²—Where the Dumas method is used, the temperatures, for the reason already given, are only approximate. Then, at 357° the dissociation pressure of ammonium chloride is about 1150 mm., so that, at 760 mm. in the open Dumas bulb at this temperature, the vapor has reached a highly unsaturated condition,

¹ THIS JOURNAL, 36, 1364 (1914).

² For a summary of previous work see Abegg. *Handb. anorg. Chem.*, Band III, 252, 265, 271.

TABLE I.—PREVIOUS DETERMINATIONS.

| Observer. | Date and method. | Temp. | Method of heating. | Vapor dens. obsd. Δ . | Per cent. dissocd. |
|---|------------------|---------------|------------------------------|------------------------------|--------------------|
| AMMONIUM CHLORIDE ($\delta = 0.00238$). | | | | | |
| Deville and Troost ¹ | 1859 | 350° | Mercury | 0.00131 | 82 |
| | D. | 1040° | Zinc | 0.00129 | 85 |
| Ramsay and Young ² | 1887 | 280° | Bromo-naphthalene, 752.3 mm. | 0.00133 | 79 |
| | H. | | | 0.00137 | 74 |
| Pullinger and Gardner ³ | 1891 | Mod. red heat | | ... | ... |
| | V. M. | | | 0.00120 | 98 |
| | V. M. | 448° | Sulfur | 0.00127 | 87 |
| | V. M. | 448° | Sulfur | 0.00121 | 97 |
| | V. M. | 360° | Anthracene | 0.00122 | 95 |
| | V. M. | 300° | α -Naphthylamine | 0.00127 | 87 |
| | V. M. | 300° | α -Naphthylamine | 0.00127 | 87 |
| | V. M. | 300° | α -Naphthylamine | 0.00127 | 87 |
| Neuberg ⁴ | 1891 | 254° | Diphenyl | 0.00146 | 63 |
| | V. M. (25 mm.) | 254° | Diphenyl | 0.00155 | 55 |
| Baker ⁵ | 1894 | 350° | Mercury | 0.00119 | 100 |
| | D. | 350° | Mercury | 0.00125 | 91 |
| Gutmann ⁶ | 1898 | 380° | Anthraquinone | 0.00122 | 95 |
| | V. M. | | | | |
| Johnson and Abegg ⁷ (see below) | 1908 | 323° | Air bath | 0.00120 | 98 |
| AMMONIUM BROMIDE ($\delta = 0.00438$). | | | | | |
| Deville and Troost ⁸ | 1863 | 440° | Sulfur | 0.00216 | 100 |
| | D. | 860° | Cadmium | 0.00221 | 98 |
| AMMONIUM IODIDE ($\delta = 0.00648$). | | | | | |
| Deville and Troost ⁸ | 1863 | 440° | Sulfur | 0.00335 | 94 |
| | D. | 860° | Cadmium | 0.00360 | 80 |

and dissociation has been favored. The fact, therefore, that values indicating 91–100% dissociation are thus obtained, does not prove that the vapor when saturated is dissociated to this extent. Similarly, in the case of ammonium bromide, a dissociation pressure of 760 mm. is reached at 394.6°, and at 445° the pressure is over 2 atmos. With ammonium iodide 760 mm. pressure is reached at 405°, and at 445° the pressure is about 2 atmos. These vapors were therefore also under greatly reduced

¹ Deville and Troost, *Ann. chim. phys.*, [3] 58, 257 (1860); *Compt. rend.*, 49, 242 (1859).

² Ramsay and Young, *Phil. Trans.*, 177, 99 (1886).

³ Pullinger and Gardner, *Proc. Chem. Soc.*, 7, 2 (1891).

⁴ Neuberg, *Ber.*, 24, 2543 (1891).

⁵ Baker, *J. Chem. Soc.*, 65, 615 (1894).

⁶ Gutmann, *Ann.*, 299, 282 (1898).

Three other observations with progressive drying of the salt (intended to delay dissociation) gave, as might be expected, higher and higher values for the density. The percentages dissociated were then 91, 79, and 61, respectively.

⁷ F. M. G. Johnson, *Z. physik. Chem.*, 61, 462 (1908).

⁸ Deville and Troost, *Compt. rend.*, 56, 895 (1863).

pressure, and the observations afford no information in regard to their degree of dissociation when saturated.

Where the Victor Meyer method was used there were two possibilities. In the first four observations of Pullinger and Gardner, in the observations of Neuberg (made under 25 mm. pressure) and in those of Gutmann, the temperature was such that the substance exercised a dissociation pressure greatly exceeding that finally existing in the apparatus. In these instances, therefore, the vapor became highly unsaturated and dissociation was favored. In the last three observations of P. and G. the dissociation pressure at 300° (252.5 mm.) was not sufficient to permit rapid vaporization and free displacement of the air (at 760 mm.). Here, therefore, the vaporization would proceed largely by diffusion of the gases into the air contained in the apparatus. Naturally, dissociation was promoted by this process of diffusion, and the displacement of air could stop only when dissociation was complete. Strictly speaking, the same thing is true of all determinations by the V. Meyer method. Every substance capable of dissociating, no matter how slightly, would be bound by this method to yield a value for the density corresponding to complete dissociation. If these observations had shown 100% dissociation, they would only have proved that the laws of equilibrium were at work, and would have given no new information about the properties of ammonium chloride.¹ Since the P. and G. determinations, for example, gave only 87% dissociation, what they did prove was that the method was inaccurate (densities 7% too low) under these conditions. The results by these two methods, apart from the obvious crudeness of the measurements, are therefore valueless for a study of the state of equilibrium in the system, because the conditions are wholly indefinite.

In the method used by F. M. G. Johnson and Abegg, the solid salt was contained in the smaller of two connected bulbs, both of which were completely evacuated. The bulbs were heated in an air bath, the larger bulb was then sealed off, and its volume and content of ammonium chloride determined. This method would have given the density of the saturated vapor, if both bulbs had been at the same temperature. But that containing the solid was intentionally kept at a temperature about 22° below that of the bulb containing the vapor. Hence, this result also applies to the unsaturated vapor, and no information about the density of the saturated vapor is obtainable from the data.

Finally, the observations of Ramsay and Young were made by the Hofmann method. They made nine determinations at 280° with pres-

¹ The fact that the facile V. Meyer method is applicable indeed to the detection of the existence of dissociation (if this has not been detected otherwise already), but is valueless for the study of the extent of such dissociation, seems to have been too generally overlooked.

tures varying from 127.3 mm. to 134.9 mm. The values quoted in the table are those obtained at these two pressures, respectively. Now the dissociation pressure at 280° is 135.0 mm., so that the last observation does yield a value for the saturated vapor. Furthermore, the observations are fairly consistent, and clearly are not in error to the extent of 20%. This observation alone, therefore, of all the published results, affords rather definite information about the density of ammonium chloride vapor in the saturated condition, and indicates that the vapor is far from being completely dissociated.

An examination of the degrees of dissociation, showing that nearly all approach 100%, within the rather wide limits of error of the methods, explains the fact that chemists have very generally accepted the erroneous conclusion that the ammonium halides are completely dissociated, and have used this incorrect assumption, for example, in calculating the heats of vaporization¹ to form saturated vapor.

Method and Apparatus.

The Vapor Density Bulbs.²—The vapor densities were determined in bulbs of the type shown in Fig. 1. A weighed amount of the substance was placed in the small bulb, A, which was then sealed on to the large bulb, B, at C. The whole was then evacuated to less than 0.01 mm. on

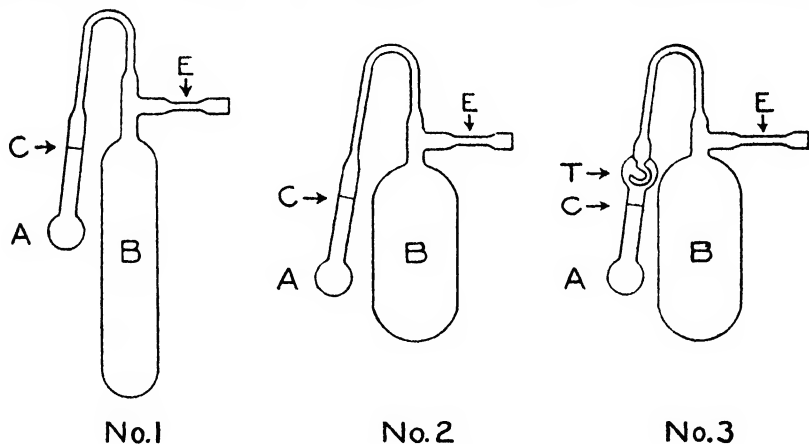


Fig. 1.—Vapor density bulbs.

a mercury pump, and sealed off from the pump at E. The evacuated bulb was next wired to a long iron rod, and then plunged into a well stirred bath having the desired temperature. Local cooling and cracking of the

¹ F. M. G. Johnson, *Z. physik. Chem.*, 65, 38 (1908-9); Horstmann, *Ber.*, 2, 137 (1869).

² Essentially the same method has been previously used by Smith and Menzies (*This Journal*, 32, 1550 (1910)) for determining the density of saturated calomel vapor.

bulb by contact with the cold iron rod were prevented by wrapping the latter with several layers of asbestos paper. When equilibrium had been reached, the large and small bulbs were sealed and separated by raising the bulb until the arched capillary just appeared above the surface of the bath and applying the blow pipe flame to it. The amount of substance which had vaporized into the large bulb was given by the difference between the amount remaining in the small bulb, and that originally put into it. The volume of the large bulb, at the temperature at which the vapor density was measured, was determined by weighing it, first evacuated and then full of water of known temperature, and finally correcting for the expansion of the glass by using the coefficient of cubical expansion, 0.000031.

Bulb No. 1 was the first type tried, and was used for determining the vapor density of ammonium chloride. The results obtained with it had an accuracy of only $\pm 2-3\%$. Hence, in the case of ammonium bromide, the vapor density of which was next measured, a more compact form of bulb, No. 2, was used, it being thought that there would be less possibility of a difference in temperature between the extreme parts of the bulb. This change, however, did not very much increase the uniformity of the results. With ammonium iodide, Bulb No. 2, gave results so erratic as to be of almost no value. The particles of the salt had a tendency to jump about, and the irregularities were in part due to the carrying over into the large bulb of solid particles of the salt by the ammonium iodide vapor when vaporization first began. To minimize this possibility, Bulb No. 3, which contained a trap T placed between the large and small bulbs, was designed. Glass wool inserted at the same place would also serve the purpose, but would necessitate determining the amount of substance in the large bulb by analysis. The results obtained with ammonium iodide with this trap were very much less erratic than without it. It may be said here that, to determine vapor densities of solids with moderate accuracy, extreme care must be exercised. Even with such care, an erratic and unaccountable result is occasionally obtained, as the results given later will show.

The Bath.—The bath was a pressed steel "oyster bucket," 18 cm. in diameter and 23 cm. deep, filled with a 50% mixture of fused sodium and potassium nitrates. Its sides were lagged by a two-inch thickness of shredded asbestos pipe-covering, and the top was covered by a sheet of $\frac{1}{2}$ " asbestos board with openings in it for the vapor-density bulb, stirrers, and thermometer. The temperature of the bath, which was heated by a Vulcan gas burner, was kept constant within $\pm 0.2-0.3^\circ$ by the constant manipulation of a screw clamp on the gas supply tube. Two stirrers of the type described by Smith and Menzies¹ were used, each rapidly

¹ Smith and Menzies, *THIS JOURNAL*, 32, 1421 (1910).

driven by an electric motor. The vapor-density bulb was in the center of the bath, the stirrers on diametrically opposite sides of the bulb, and the thermometer directly behind the bulb.

Measurement of the Temperature.—The temperature of the bath was measured by a fused quartz, platinum resistance thermometer of the Heraeus type¹ without compensating leads. The resistance of the thermometer was measured by a dial Wheatstone bridge (5 dials), and a D'Arsonval galvanometer, both manufactured by the Leeds & Northrup Co.

The thermometer was calibrated, by the method recommended by Waidner and Burgess,² at the melting point of ice, and at the boiling points of water and of sulfur (444.7°). The steam point was determined in a glass tube 5 cm. in diameter, and 46 cm. long, heated by a Vulcan gas burner, and lagged by a conical asbestos jacket 2 cm. thick at the top, 6 cm. thick at the bottom, and 32 cm. high. The depth of water in the tube was about 10–12 cm., the bottom of the thermometer was about 4 cm. above the surface of the water, and glass beads were used to prevent bumping. An aluminum radiation shield, of the type recommended by Waidner and Burgess, was used. The sulfur boiling point tube was of brass, 4.7 cm. in diameter, and 47 cm. long. A depth of 10–12 cm. of sulfur were used, and the end of the thermometer was placed about 4 cm. above the surface of the boiling sulfur. Two mica windows at the top of the tube made it possible to observe the point of condensation of the sulfur vapor. This was kept about half way between the top of the tube and the top of the jacket. The asbestos insulating jacket and aluminum radiation shield described above were used.

In order to test the accuracy of the calibration, the boiling point of naphthalene was determined several times. The results were usually about 0.2° higher than the value given by Waidner and Burgess.³ This is probably as good a result as could be expected without using compensating leads. The constants of the thermometer increased gradually during the investigation, but the change was followed closely, and new values were adopted as soon as the difference became great enough to cause an error of as much as 0.1–0.2° in the temperature measurement. The accuracy and constancy of the temperature of the bath is estimated to have been about ± 0.2 – 0.3° .

Ammonium Chloride.

The Data.—The ammonium chloride was recrystallized once from distilled water, dried at 110°, finely ground, and kept in a desiccator over

¹ Waidner and Burgess, "The Measurement of High Temperatures" (Wiley, 3rd ed.) 205.

² Waidner and Burgess, *Bull. Bur. Standards*, 6, 150 (1910).

³ *Ibid.*, 7, 4 (1910).

phosphorus pentoxide. The vapor density was determined at ten-degree intervals from 280° to 330° , the first temperature being that at which the vapor density becomes large enough to be accurately measured, and the second that at which the dissociation pressure becomes almost equal to atmospheric pressure. The pressure of the ammonium chloride vapor in the bulb must not be allowed to become greater than atmospheric because, if it did, the capillary tube between the large and small bulbs would blow out instead of collapsing, when the two bulbs were sealed apart.

In order to obtain a final, mean result which was sufficiently accurate, it was necessary to make a number of determinations at each temperature. In order that the degree of accuracy of the measurements may be clearly seen, the results of all the determinations made are given (Table II). The volumes (Col. 3 of the table) are at the temperature at which the vapor density determination was made. The column entitled "deviation from mean" contains the difference between the average value of the vapor density and the individual measurements. Occasionally a vapor density would be obtained which was so far from the average value that we have felt justified in rejecting it. Such values are printed in italics. The precision of the average value at each temperature was obtained by averaging the "deviations from the mean," and then dividing the average by the square root of the number of observations. It will be seen that the final results usually have an accuracy of about $\pm 2-3\%$.

TABLE II.—DENSITIES OF NH_4Cl VAPOR (SATURATED)—DATA.

| Temp. | G. NH_4Cl in large bulb. | Vol. (cc.) of large bulb. | Vapor dens. g. per cc. | Deviation from mean. | Minutes in bath. |
|---------------|--|---------------------------|------------------------|--------------------------|------------------|
| 280° | 0.0081 | 54.71 | 0.000148 | +13 | 15 |
| | 0.0068 | 61.80 | 0.000110 | -25 | 15 |
| | 0.0088 | 64.65 | 0.000136 | + 1 | 15 |
| | 0.0073 | 59.39 | 0.000123 | -12 | 21 |
| | 0.0084 | 55.46 | 0.000151 | +16 | 20 |
| | 0.0099 | 66.21 | 0.000150 | +15 | 20 |
| | 0.0075 | 53.16 | 0.000141 | + 6 | 20 |
| | 0.0079 | 61.21 | 0.000129 | - 6 | 20 |
| | 0.0076 | 61.39 | 0.000124 | -11 | 20 |
| | Average vapor density..... | | 0.000135 | ± 4 , or $\pm 2.9\%$ | |
| 290° | 0.0098 | 64.67 | 0.000152 | -17 | 15 |
| | 0.0102 | 65.48 | 0.000156 | -13 | 15 |
| | 0.0095 | 61.05 | 0.000156 | -13 | 15 |
| | 0.0110 | 63.15 | 0.000174 | + 6 | 15 |
| | 0.0103 | 60.87 | 0.000169 | 00 | 20 |
| | 0.0110 | 63.97 | 0.000173 | + 4 | 20 |
| | 0.0132 | 67.27 | 0.000196 | +27 | 20 |
| | 0.0110 | 66.05 | 0.000167 | - 2 | 20 |
| | 0.0116 | 67.21 | 0.000177 | + 8 | 20 |
| | 0.0111 | 64.66 | 0.000172 | + 3 | 20 |
| | Average vapor density..... | | 0.000169 | ± 3 , or $\pm 1.8\%$ | |

TABLE II.—DENSITIES OF NH_4Cl VAPOR (SATURATED)—DATA (*continued*).

| Temp. | G. NH_4Cl in large bulb. | Vol. (cc.) of large bulb. | Vapor dens. g. per cc. | Deviation from mean. | Minutes in bath. |
|----------------------------|--|---------------------------|------------------------|----------------------|------------------|
| 300° | 0.0160 | 65.09 | 0.000246 | +16 | 11 |
| | 0.0153 | 63.43 | 0.000242 | +12 | 11 |
| | 0.0146 | 64.75 | 0.000226 | — 6 | 12 |
| | 0.0122 | 59.83 | 0.000204 | —26 | 13 |
| | 0.0113 | 65.84 | 0.000172 | .. | 13 |
| | 0.0167 | 74.23 | 0.000225 | — 5 | 10 |
| | 0.0150 | 62.55 | 0.000240 | +10 | 13 |
| Average vapor density..... | | | 0.000230 | ±5, or 2.2% | |
| 310° | 0.0229 | 71.19 | 0.000322 | +15 | 13 |
| | 0.0161 | 62.70 | 0.000257 | .. | 10 |
| | 0.0217 | 70.44 | 0.000308 | + 1 | 12 |
| | 0.0203 | 62.45 | 0.000325 | +18 | 11 |
| | 0.0169 | 62.09 | 0.000272 | .. | 13 |
| | 0.0186 | 59.66 | 0.000312 | + 5 | 12 |
| | 0.0185 | 63.68 | 0.000291 | —16 | 12 |
| | 0.0182 | 56.26 | 0.000324 | +17 | 13 |
| | 0.0194 | 66.37 | 0.000292 | —15 | 12 |
| | 0.0166 | 54.40 | 0.000305 | — 2 | 11 |
| | 0.0200 | 70.93 | 0.000282 | —25 | 12 |
| Average vapor density..... | | | 0.000307 | ±4, or ±1.3% | |
| 320° | 0.0255 | 61.94 | 0.000413 | + 7 | 11 |
| | 0.0248 | 60.51 | 0.000410 | + 4 | 12 |
| | 0.0282 | 71.66 | 0.000394 | —12 | 12 |
| | 0.0274 | 67.33 | 0.000407 | + 1 | 11 |
| Average vapor density..... | | | 0.000406 | ±3, or ±0.7% | |
| 330° | 0.0330 | 66.93 | 0.000493 | —38 | 20 |
| | 0.0330 | 70.07 | 0.000471 | .. | 15 |
| | 0.0387 | 68.77 | 0.000563 | +32 | 18 |
| | 0.0424 | 74.63 | 0.000568 | +37 | 17 |
| | 0.0321 | 65.25 | 0.000492 | —39 | 17 |
| | 0.0291 | 63.87 | 0.000456 | .. | 12 |
| | 0.0348 | 63.50 | 0.000548 | +17 | 11 |
| | 0.0302 | 56.66 | 0.000533 | + 2 | 13 |
| | 0.0345 | 62.65 | 0.000551 | +20 | 13 |
| | 0.0366 | 68.16 | 0.000537 | + 6 | 11 |
| | 0.0297 | 66.64 | 0.000446 | .. | 11 |
| | 0.0343 | 66.68 | 0.000514 | —17 | 11 |
| | 0.0271 | 53.75 | 0.000504 | —27 | 12 |
| | 0.0323 | 59.94 | 0.000539 | + 8 | 11 |
| Average vapor density..... | | | 0.000531 | ±6, or ±1.3% | |

In Table III are summarized the vapor density results in the form in which they were used in the calculations. The vapor pressures given in this table are those determined by Smith and Calvert.¹ The method for, and the purpose of determining the "interpolated" values given in the fifth column will be explained when the calculation of the dissociation

¹ Smith and Calvert, *THIS JOURNAL*, 36, 1373 (1914).

constants is discussed. The densities, δ_m , which the vapor would have if it were undissociated (expressed in mols per liter), and yet gave the measured dissociation pressures were calculated by the formula

$$\delta_m = \frac{1}{22.4} \cdot \frac{273}{T} \cdot \frac{P}{760}$$

These values are given in the column headed, "undissociated." In the column headed, "completely dissociated," are the densities which the vapor would have if it were wholly dissociated and gave the measured dissociation pressure. These values are just one-half of the corresponding "undissociated" vapor densities.

In order to show the relation between the measured vapor density and the density of the vapor if it were completely dissociated, and if undissociated, these values have been plotted in Fig. 2. The fact that

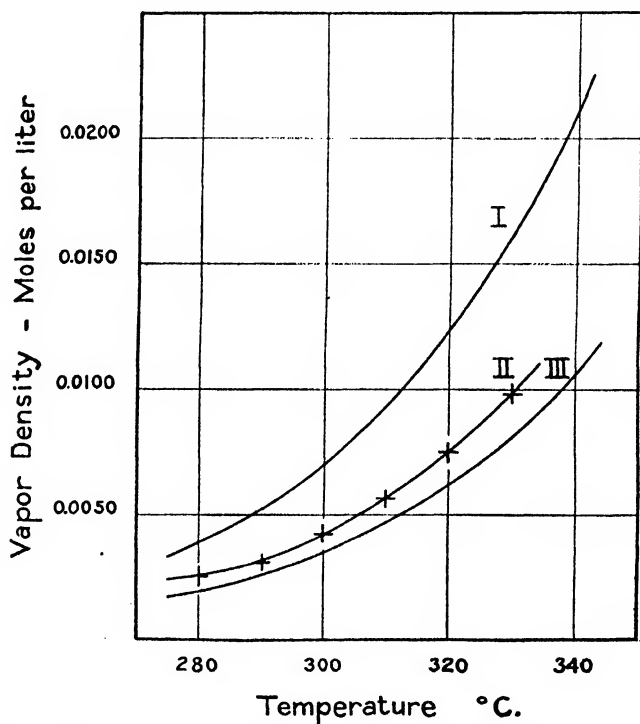


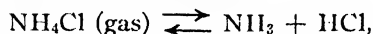
Fig. 2.—Vapor densities of ammonium chloride: Curve I—Undissociated (calculated); Curve II—Observed; Curve III—Completely dissociated (calculated).

the experimentally determined values lie between the "undissociated" and the "completely dissociated" densities, shows conclusively that saturated ammonium chloride vapor is not completely dissociated. If it were completely dissociated, the measured values would lie, at least approximately, on the "completely dissociated" curve.

TABLE III.—DENSITIES OF NH_4Cl VAPOR (SATURATED)—SUMMARY.

| | | Vapor density. | | | | | Total press. Mm. |
|-------|------|----------------|-----------------------------|--|--|----------------------------------|------------------------|
| | | Observed. | | Calculated. | | | |
| Temp. | | G. per cc. | Mols per l. Δm . | Interpol. Mols per l. Δm_i . | Undissoc. Mols per l. δm . | Compl. dissoc. Mols per l. | |
| C. | Abs. | | | | | | |
| 280 | 553 | 0.000135 | 0.00252 | 0.00235 | 0.00392 | 0.00196 | 135.0 |
| 290 | 563 | 0.000169 | 0.00316 | 0.00318 | 0.00528 | 0.00264 | 185.3 |
| 300 | 573 | 0.000230 | 0.00430 | 0.00428 | 0.00707 | 0.00354 | 252.5 |
| 310 | 583 | 0.000307 | 0.00573 | 0.00571 | 0.00939 | 0.00470 | 341.3 |
| 320 | 593 | 0.000406 | 0.00759 | 0.00757 | 0.01239 | 0.00620 | 458.1 |
| 330 | 603 | 0.000531 | 0.00993 | 0.00998 | 0.01624 | 0.00812 | 610.6 |
| 340 | 613 | | | | 0.02114 | 0.01067 | 808.2 |

The Degrees of Dissociation.—In calculating the degree of dissociation of ammonium chloride vapor, it was assumed that the equilibrium present in the vapor is represented by the equation



and that the gases follow the laws of perfect gases. If so, the degree of dissociation α is given by the formula

$$\alpha = \frac{\delta m - \Delta m}{\Delta m}.$$

In this formula, δm , and Δm , are respectively the "undissociated," and the observed molar vapor densities (Table III). The degrees of dissociation thus calculated are given in Table IV (Col. 2).

TABLE IV.— NH_4Cl —DEGREES OF DISSOCIATION.

| Temp. C. | Percentage dissociation. | | Deviation of α from straight line. | | % error in α . (Calcd.) |
|-------------|--------------------------|-----------|--|-------|-----------------------------------|
| | Obsd. | Interpol. | Actual. | %. | |
| 280 | 55.5 | 66.8 | ... | ... | ... |
| 290 | 67.1 | 66.0 | +1.1 | +1.7 | ± 4.5 |
| 300 | 64.2 | 65.2 | -1.0 | -1.5 | ± 5.5 |
| 310 | 63.8 | 64.4 | -0.6 | -0.93 | ± 3.5 |
| 320 | 63.3 | 63.6 | -0.3 | -0.47 | ± 1.8 |
| 330 | 63.6 | 62.8 | +0.8 | +1.3 | ± 3.3 |

Inasmuch as the measured results are somewhat irregular,¹ the relation between the degree of dissociation and the temperature is seen best from the graphic representation of the results given by Fig. 3, Curve I. This curve shows that between 280° and 330°, saturated ammonium chloride vapor is 67–63% dissociated; and that, although the degree of dissociation is very nearly constant, it apparently decreases slightly and, as nearly

¹ The irregularities in our results might be attributed to adsorption of the vapors by the surface of the bulbs, or might be connected with the existence of transition points for ammonium chloride and bromide at 159° and 109°, respectively (Wallace, *Chem. Zentr.*, 81, 727 (1910)). In view of the fact that our measurements were made at relatively high temperatures, usually 300° and above, these explanations must be discarded.

as can be judged, linearly with the temperature. In view of the irregularity of the measured values of α , we shall use hereafter in any calculations which involve α , values interpolated from Curve I in Fig. 3. These values are given in the third column of Table IV.

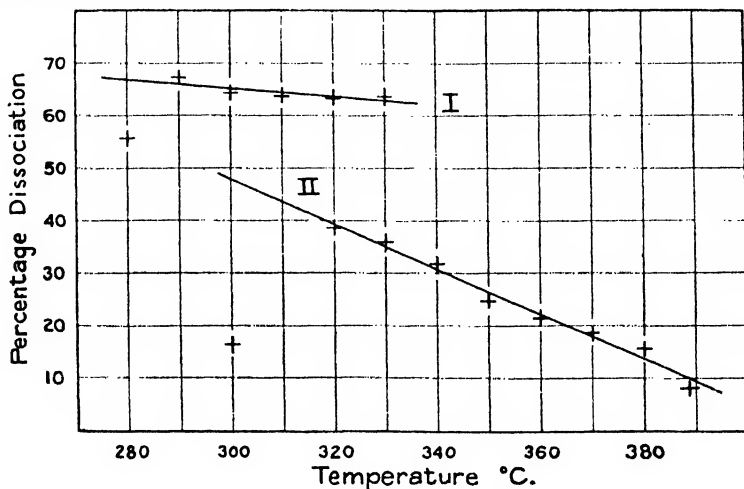


Fig. 3.—Percentage dissociation of saturated ammonium chloride and bromide vapors: Curve I—Ammonium chloride; Curve II—Ammonium bromide.

The irregularity of α is not, however, more than might be expected, because the relation between α and Δ_m is of such a nature that an error in Δ_m is multiplied several times in α . To illustrate this, we give the errors in the values of α which might be expected, and compare these with the actual errors. The error in α which would be caused by an error in Δ_m may be calculated as follows: If $d\Delta_m$ is the error in Δ_m , the error in α , will be,

$$\frac{\partial \alpha}{\partial \Delta_m} d\Delta_m = \frac{\partial}{\partial \Delta_m} \left[\frac{\delta_m - \Delta_m}{\Delta_m} \right] d\Delta_m = -\frac{\delta_m}{\Delta_m^2} d\Delta_m,$$

and the percentage error in α will be,

$$\frac{\partial \alpha / \partial \Delta_m d\Delta_m}{\alpha} = \frac{-\delta_m / \Delta_m^2 d\Delta_m}{\delta_m - \Delta_m / \Delta_m} = -\frac{\delta_m}{\delta_m - \Delta_m} \frac{d\Delta_m}{\Delta_m}$$

But $\frac{d\Delta_m}{\Delta_m}$ is the percentage error in Δ_m . Therefore,

$$(\% \text{ error in } \alpha) = -(\% \text{ error in } \Delta_m) \frac{\delta_m}{\delta_m - \Delta_m}.$$

In the sixth column of Table IV are given the percentage errors in α , calculated by this equation, which would result from the percentage errors in Δ_m which are given in Table II. The actual errors in α , i. e., the deviation of the observed values of α from the average values, are

given by the difference between the observed values of α and the value interpolated from the straight line. These differences are given in the fourth column of Table IV, and the fifth column contains these differences expressed as percentages of the observed value of α . Comparison of Columns 5 and 6 shows that the percentage deviation of α from a straight line is much less than might be expected to result from the errors in Δ_m . Therefore, a straight line represents the relation between the degree of dissociation and the temperature within the experimental error of the observations. The value of α at 280° , which is obviously too low, was not considered when the best representative straight line was drawn.

The fact that the vapor density increases and that the degree of dissociation *diminishes* with rising temperature, is at first sight anomalous. It must be remembered, however, that the results are not obtained with constant total pressure (as in the Dumas and V. Meyer methods) but with rapidly rising total pressure (vapor pressure). Thus between 290° and 330° the partial pressure of free ammonia (or HCl, see Table XV) rises from 73.7 mm. to 234.5 mm., while the total pressure increases from 185.3 mm. to 610.6 mm., or almost in the same proportion. If we calculate the change in partial pressure of free ammonia which would occur between the same limits of temperature if the total pressure were kept constantly at 185.3 mm., we find that this partial pressure would rise from 73.7 to 83.6 mm. Thus at a constant pressure of 185.3 mm., the density would diminish and the degree of dissociation would *increase* from 66% to 82%.

The Latent Heat of Vaporization.—Several determinations of the latent heat of vaporization of ammonium chloride have previously been attempted, but none of them gives the true latent heat of vaporization, namely, the heat-change involved when ammonium chloride vaporizes in equilibrium with the products of its vaporization. These previous determinations are summarized in Table V.

TABLE V.— NH_4Cl —LATENT HEATS OF VAPORIZATION (Kg. cal. per mol).

| Observer. | Date. | Temp. | $\frac{L}{\text{Kg. cal.}}$ |
|-------------------------------------|-------|---------|-----------------------------|
| Marignac ¹ | 1869 | 420–500 | 37.8 |
| Horstmann ² | 1869 | 340 | 37.4 |
| Horstmann..... | 1869 | 300 | 39.5 |
| Horstmann..... | 1869 | 260 | 41.4 |
| Horstmann..... | 1869 | 220 | 43.9 |
| F. M. G. Johnson ³ | 1909 | 245–345 | 37.8 |

¹ Marignac, Liebig's *Ann.*, **149**, 351 (1869).

² Horstmann, *Ber.*, **2**, 137 (1869).

³ F. M. G. Johnson, *Z. physik. Chem.*, **65**, 38 (1908–9); Favre and Silbermann (*Ann. chim. phys.*, [3] **37**, 422 (1853)), and J. Thomsen (*Thermochem. Untersuch.*, Leipzig, Band II, 73–75 (1889)) have found the values 39.7 and 41.3, respectively, for the heat of reaction between ammonia and hydrogen chloride

Horstmann and F. M. G. Johnson calculated the latent heat of vaporization from their respective vapor pressure data, the former using the Clausius-Clapeyron equation, and the latter the relation, $d \ln p/dT = Q/2RT^2$. Both, however, made the incorrect assumption that saturated ammonium chloride vapor is completely dissociated. Hence, their results must be larger than the correct values.

Marignac's experimental method was admittedly rather inaccurate, the measurements were made at atmospheric pressure, and the value for the latent heat of vaporization given in Table V is the mean of two extreme values, 33.0 and 43.8. Since his measurements were not made under equilibrium conditions, the results have little quantitative significance.

Previous observers have, therefore, failed to obtain correct values for the latent heat of vaporization of ammonium chloride, either because they have not worked under equilibrium conditions, or because, in the absence of data in regard to the densities of the saturated vapor, they have uncritically assumed complete dissociation.

Neither of these objections, however, applies to the method which we have used, because we have calculated the molar latent heat of vaporization from the dissociation pressures and the saturated vapor densities, using the Clausius-Clapeyron equation, $L = T \partial P/\partial T (V - v)$. In this equation, v , the molar volume of the solid, is negligible; and the molar volume of the vapor V is equal to $1/\Delta_{mi}$. The value of $\partial P/\partial T$ was found from the Kirchoff-Rankin-Dupré equation

$$\log P = -A/T + B \log T + C,$$

in which the constants, A , B , and C have been evaluated for the ammonium halides by Smith and Calvert.¹ When this equation is solved for P , and the resulting value of P is differentiated with respect to T , it is found that,

$$\frac{\partial P}{\partial T} = P \left[\frac{A}{0.4343 T^2} + \frac{B}{T} \right].$$

Substituting now in the Clausius-Clapeyron equation these expressions for V , and $\partial P/\partial T$ gives

$$L = T \frac{P}{760} \left[\frac{A}{0.4343 T^2} + \frac{B}{T} \right] \frac{0.02419}{\Delta_{mi}} \text{ Kg. cal.}$$

P is the dissociation pressure of ammonium chloride in mm. of mercury, and Δ_{mi} is the interpolated molar vapor density, both as given in Table III. $A = 1920$, and $B = 9.779$.

at room temperature. Johnson incorrectly quotes these data as heats of vaporization, and compares his values of the latent heat of vaporization with them.

¹ Smith and Calvert, *THIS JOURNAL*, 36, 1368, 1371, 1373 (1914).

Using this formula, the following values of the molar latent heats of vaporization between 280° and 330° were obtained:

| NH ₄ Cl—LATENT HEATS OF VAPORIZATION (Kg. cal. per mol). | | | | | |
|---|------|------|------|------|------|
| 280° | 290° | 300° | 310° | 320° | 330° |
| 32.5 | 32.7 | 32.9 | 33.0 | 33.2 | 33.3 |
| Average value..... | | 32.9 | | | |

Since the extreme values differ only by about 1% from the average value, it may be assumed that the latent heat of vaporization of ammonium chloride between 280° and 330° is constant within the experimental error. That the average value is smaller than the older values given in Table V is to be expected, because, as explained above, the latter were obtained by methods which would necessarily yield results larger than the correct value.

The Dissociation Constant.—For calculating the heats of dissociation, it is necessary to determine the dissociation constants of ammonium chloride at different temperatures. The dissociation constant K_c is given

by the equation

$$K_c = \frac{\alpha^2}{1-\alpha} \Delta_{mi}.$$

First, a series of values of K_c was calculated, using the observed molar vapor densities Δ_m (Table III), and the observed values of α (Table IV). The values of the dissociation constant thus determined are the "observed" values given in Table VI, and they are represented graphically by the points which lie on either side of the curve in Fig. 4. They are, of course, somewhat irregular because of the experimental errors in Δ_m and, especially, in α .

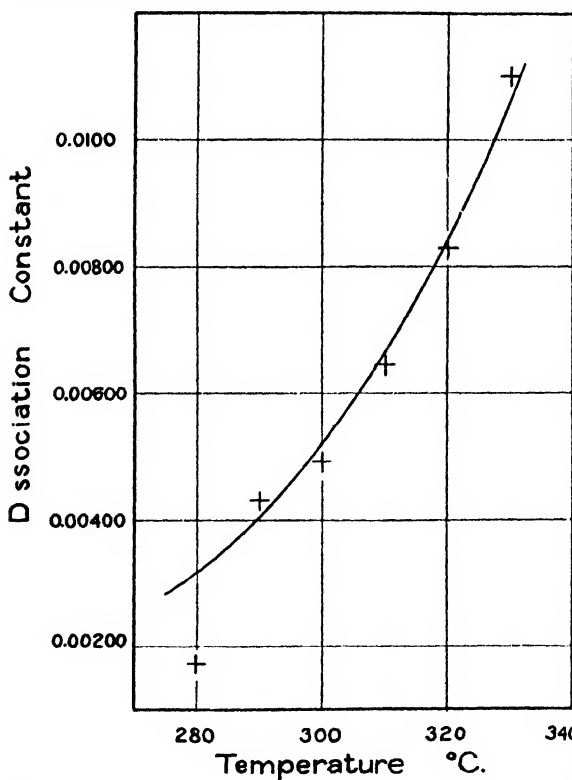


Fig. 4.—Dissociation constants of saturated ammonium chloride vapor.

In order to get a smooth, average set of values of K_c , a second series of values was calculated,

using the interpolated values of α , given in Table IV, and the "interpolated" vapor densities, Δ_{mi} (Table III). Δ_{mi} was calculated by the formula

$$\Delta_{mi} = \frac{\delta}{1 + \alpha_{interpol.}},$$

and is simply the density which the saturated vapor would have if it gave the interpolated values of α instead of the measured values. This second series of values of K_c is that entitled "average" in Table VI, and they lie directly on the curve in Fig. 4.

TABLE VI.— NH_4Cl —DISSOCIATION CONSTANTS— K_c .

| Temp. | 280°. | 290°. | 300°. | 310°. | 320°. | 330°. |
|---------------|---------|---------|---------|---------|---------|--------|
| Observed..... | 0.00174 | 0.00432 | 0.00496 | 0.00644 | 0.00828 | 0.0110 |
| Average..... | 0.00316 | 0.00407 | 0.00523 | 0.00665 | 0.00842 | 0.0106 |

The difference between the observed and the "average" values of K_c is, in some cases, rather large, but not greater than would be expected from the nature of the relation between K_c and α , and the error in α . Fig. 4 shows that the "average" values of K_c , as represented by the curve, are the best possible average of the observed values. These "average" values of K_c will be used in calculating the heat of dissociation rather than the observed values.

The Heat of Dissociation—General.—The fundamental relation between the heat evolved during dissociation, and the dissociation constant is expressed by the van't Hoff equation

$$\frac{d \ln K_c}{dT} = - \frac{U}{RT^2}.$$

U is the heat which would be evolved if one mol of substance, *e. g.*, ammonium chloride vapor, dissociated isothermally, without performing external work. In order to integrate this equation it is necessary to decide upon the nature of the relation between U and T . The exact relation not being known, it has been customary to employ an interpolation formula of the type

$$U = A + BT + CT^2 + DT^3 + \dots \quad (\text{I})$$

where A, B, C, D, \dots are constants. Lundén,¹ in the calculation of heats of ionization, has used the condensed form,

$$U = A + BT, \quad (\text{II})$$

disregarding powers of T higher than the first. This, however, is not in agreement with Nernst's heat theorem, which postulates the relation,

$$dU_0/dT = \text{zero.} \quad (U_0 = U \text{ at absolute zero.})$$

The equation used by Lundén gives $dU_0/dT = B$. Hence, it is evident that in Equation I above, $B = \text{zero}$.

¹ Lundén, *J. chim. phys.*, 5, 593 (1907).

The representation of U in expanding powers of T has recently been studied by Arrhenius.¹ We have, from the second law of thermodynamics,

$$U = A - TdA/dT \quad (A = \text{free energy}).$$

Hence, if we assume A represented in expanding powers of T , *i. e.*,

$$A = A_0 + BT + CT^2 + DT^3 + \dots$$

we have also,

$$T dA/dT = BT + 2CT^2 + 3DT^3 + \dots$$

and consequently, by subtraction,

$$U = A_0 - CT^2 - 2DT^3 - \dots \quad (\text{III})$$

Now Arrhenius has shown that in this equation, if we do not consider very high temperatures, all powers of T above the second may be disregarded. The resultant equation,

$$U = A_0 - CT^2$$

is very widely applicable, and has been proved to hold for many different types of reactions through large ranges of temperature. Nevertheless, it must always be carefully borne in mind that the equation is, in the end, only an approximation, being a condensed form of the expanding series shown in (III), and breaking down if its limits are overstepped. Strictly speaking, the equation is also dependent upon the gas laws, and should be applied only if they hold exactly. The practical range, however, is much wider, and it can be used with success in many cases where the gas laws do not even approximately apply. In such instances it must be considered to be merely an interpolation formula, and in this character it may be employed in the present investigation. Examination of our experimental results shows that, for them, the equation used by Lundén does not hold. With the equation of Arrhenius, however, satisfactory agreement can be obtained, in the case of ammonium chloride, throughout the available temperature range.

The Heat of Dissociation of NH_4Cl .—The heat of dissociation of ammonium chloride vapor has not been determined previously because the values of the dissociation constant at different temperatures are necessary for its calculation, and they have never been determined.

By combining Arrhenius' formula with the van't Hoff equation, there is obtained

$$d \ln K_c = - \frac{A_0}{RT^2} dt + \frac{C}{R} dT$$

and integration of this equation yields,

$$4.571 \frac{\log K_{c1} - \log K_{c2}}{T_1 - T_2} = - \frac{A_0}{T_1 T_2} + C. \quad (\text{IV})$$

¹ Arrhenius, "Energieverhältnisse bei Dampfbildung und bei elektrolytischer Dissoziation," *Meddel. från K. Vet. Akad. Nobelinstitut*, Band 2, No. 8.

From Equation IV the values of A_0 and of C may be found by solving the two simultaneous equations obtainable from the values of K_c at any three different temperatures; but we have used the following graphic method which is more general and more accurate. If Equation IV is written in the form,

$$y = -A_0x + C,$$

it is evident that it is the equation of a straight line. From each pair of values of K_c which is available from the data, and the corresponding temperatures, a value of both y and x may be obtained. If these values of y and x are plotted they will lie on a straight line, providing Equation IV represents the correct relation between U and T . The slope of this line will be A_0 , and its intercept on the y -axis will be C . From the fifteen possible pairs of the "average" values of K_c given in Table VI, we calculated fifteen values of x and y . These were then plotted, and the best

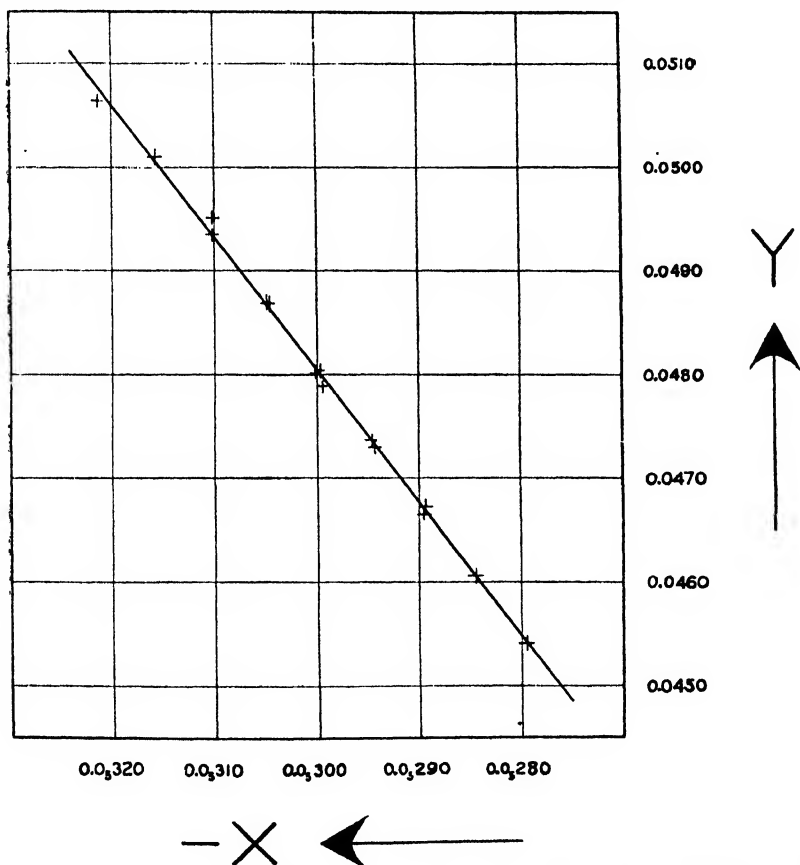


Fig. 5.—Calculation of the heat of dissociation of saturated ammonium chloride vapor. Plot of the equation, $y = -A_0x + C$.

representative straight line was drawn through them, as shown in Fig. 5. A_0 , the slope of this line, was found to be -12800 , and C , the intercept on the y -axis had the value 0.00967 , whence,

$$U = -12800 - 0.00967T^2 \text{ gram calories per mol.}$$

The fact that the results lie so well along a straight line shows that the van't Hoff equation, in conjunction with Arrhenius' relation between U and T , correctly represents the facts in the case of ammonium chloride. It is also to be noticed that the heat absorbed during dissociation increases as the temperature increases. This indicates that the molar heat of ammonium chloride vapor is less than the sum of the molar heats of its products of dissociation, and this conclusion is in accordance with the kinetic theory of gases.

Ammonium Bromide.

The Data.—The densities of saturated ammonium bromide vapor were determined between 300° and 388° , the range of temperature being determined by the same factors as in the case of ammonium chloride. Vapor density bulbs of type No. 2 (Fig. 1) were used, except at 300° and 388° . At these temperatures the "trap bulb," Fig. 1, No. 3, was employed. The ammonium bromide was recrystallized once from distilled water, then sublimed in a large evacuated glass tube, and finely pulverized.

TABLE VII.—DENSITIES OF NH_4Br VAPOR (SATURATED)—DATA.

| Temp. | G. NH_4Br in large bulb | Vol. (cc.) of large bulb. | Vapor dens. g. per cc. | Deviation from mean. | Minutes in bath. |
|----------------------------|---|---------------------------|------------------------|----------------------------|------------------|
| 300° | 0.0102 | 78.51 | 0.000130 | 0 | 30 |
| | 0.0105 | 81.49 | 0.000129 | — 1 | 30 |
| | 0.0102 | 78.04 | 0.000131 | + 1 | 30 |
| | 0.0096 | 72.83 | 0.000132 | + 2 | 30 |
| | 0.0087 | 68.64 | 0.000127 | — 3 | 30 |
| | 0.0104 | 79.23 | 0.000131 | + 1 | 30 |
| Average vapor density..... | | | 0.000130 | ± 0.5 , or $\pm 0.4\%$ | |
| 320° | 0.0134 | 72.18 | 0.000186 | — 6 | 60 |
| | 0.0155 | 81.71 | 0.000190 | — 2 | 60 |
| | 0.0135 | 67.27 | 0.000201 | + 9 | 60 |
| | 0.0141 | 73.18 | 0.000192 | 0 | 60 |
| Average vapor density..... | | | 0.000192 | ± 2 , or $\pm 1.0\%$ | |
| 330° | 0.0190 | 65.06 | 0.000292 | +33 | 60 |
| | 0.0256 | 68.61 | 0.000373 | .. | 60 |
| | 0.0173 | 69.79 | 0.000248 | —11 | 60 |
| | 0.0159 | 67.17 | 0.000237 | —22 | 60 |
| | 0.0214 | 71.62 | 0.000299 | +40 | 60 |
| | 0.0179 | 71.37 | 0.000251 | — 8 | 60 |
| | 0.0189 | 75.17 | 0.000252 | — 7 | 60 |
| | 0.0248 | 76.83 | 0.000323 | .. | 60 |
| | 0.0182 | 78.00 | 0.000233 | —26 | 60 |
| | 0.0181 | 70.31 | 0.000258 | — 1 | 60 |
| Average vapor density..... | | | 0.000259 | ± 6 , or $\pm 2.3\%$ | |

TABLE VII.—DENSITIES OF NH_4Br VAPOR (SATURATED)—DATA (*continued*).

| Temp. | G. NH_4Br in large bulb. | Vol. (cc.) of large bulb. | Vapor dens. g. per cc. | Deviation from mean. | Minutes in bath. |
|----------------------------|--|---------------------------|------------------------|----------------------|------------------|
| 340° | 0.0256 | 66.97 | 0.000382 | +34 | 60 |
| | 0.0205 | 60.46 | 0.000339 | — 9 | 60 |
| | 0.0228 | 66.74 | 0.000342 | — 6 | 60 |
| | 0.0338 | 78.72 | 0.000429 | .. | 60 |
| | 0.0255 | 74.87 | 0.000341 | — 7 | 60 |
| | 0.0295 | 71.81 | 0.000411 | .. | 60 |
| | 0.0256 | 78.02 | 0.000328 | —20 | 60 |
| | 0.0238 | 66.44 | 0.000358 | +10 | 60 |
| Average vapor density..... | | | 0.000348 | ± 6, or ±1.7% | |
| 350° | 0.0429 | 81.96 | 0.000524 | .. | 60 |
| | 0.0334 | 66.74 | 0.000496 | +18 | 60 |
| | 0.0359 | 73.32 | 0.000490 | +12 | 60 |
| | 0.0335 | 71.81 | 0.000466 | —12 | 60 |
| | 0.0349 | 72.51 | 0.000481 | + 3 | 60 |
| | 0.0321 | 69.90 | 0.000459 | —19 | 60 |
| Average vapor density..... | | | 0.000478 | ± 6, or ±1.2% | |
| 360° | 0.0435 | 66.65 | 0.000653 | +20 | 60 |
| | 0.0388 | 62.70 | 0.000619 | —14 | 60 |
| | 0.0522 | 65.54 | 0.000797 | .. | 60 |
| | 0.0473 | 77.71 | 0.000609 | —24 | 60 |
| | 0.0530 | 80.54 | 0.000658 | +25 | 60 |
| | 0.0419 | 66.99 | 0.000626 | — 7 | 60 |
| | 0.0378 | 68.72 | 0.000550 | .. | 60 |
| | 0.0469 | 74.08 | 0.000633 | 00 | 60 |
| Average vapor density..... | | | 0.000633 | ± 6, or ±1.0% | |
| 370° | 0.0565 | 68.63 | 0.000823 | —13 | 60 |
| | 0.0512 | 60.53 | 0.000846 | +10 | 60 |
| | 0.0758 | 74.68 | 0.00102 | .. | 60 |
| | 0.0566 | 67.59 | 0.000837 | + 1 | 60 |
| | 0.0705 | 74.77 | 0.000943 | .. | 60 |
| | 0.0366 | 72.31 | 0.000506 | .. | 60 |
| Average vapor density..... | | | 0.000836 | ± 5, or ±0.6% | |
| 380° | 0.0783 | 77.43 | 0.00101 | — 9 | 60 |
| | 0.0725 | 61.53 | 0.00118 | + 8 | 60 |
| | 0.0724 | 64.92 | 0.00112 | + 2 | 60 |
| | 0.0837 | 77.41 | 0.00108 | — 2 | 60 |
| Average vapor density..... | | | 0.00110 | ± 3, or ±2.7% | |
| 388° | 0.0946 | 68.72 | 0.00138 | — 4 | 30 |
| | 0.0987 | 66.36 | 0.00149 | + 7 | 30 |
| | 0.1044 | 74.11 | 0.00141 | — 1 | 30 |
| | 0.0996 | 71.95 | 0.00139 | — 3 | 30 |
| | 0.1030 | 71.47 | 0.00144 | + 2 | 30 |
| | 0.1135 | 80.33 | 0.00141 | — 1 | 30 |
| Average vapor density..... | | | 0.00142 | ± 1.2, or ±0.9% | |

The data of the individual vapor density determinations are presented in Table VII. For an explanation of this table see the discussion that

precedes Table II (ammonium chloride), which is identical in form. The accuracy of the ammonium bromide data is the same as in the case of the ammonium chloride, namely, about $\pm 2\%$.

In Table VIII are given the densities of saturated ammonium bromide vapor in the form in which they were used in the calculations. This table corresponds to Table III (ammonium chloride), and the explanation which precedes Table III applies also to it.

In order to facilitate the comparison of the observed vapor densities with the "completely dissociated" and the "undissociated" vapor densities, these have been plotted in Fig. 6.

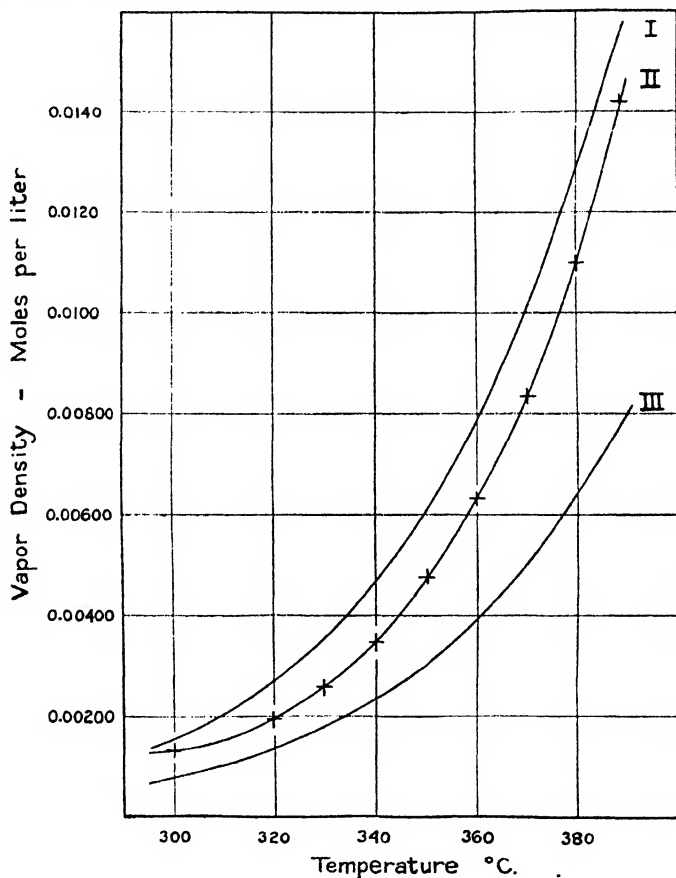


Fig. 6.—Vapor densities of ammonium bromide: Curve I—Undissociated (calculated); Curve II—Observed; Curve III—Completely dissociated (calculated).

It will be seen that the observed vapor densities lie between the "completely dissociated" and the "undissociated" densities throughout the range of temperatures studied. This fact indicates that ammonium

bromide vapor is dissociated, although not completely. Furthermore, the measured vapor densities of ammonium bromide lie much nearer to the "undissociated" curve than do the measured densities of ammonium chloride (Fig. 2), so that ammonium bromide vapor is less dissociated than is ammonium chloride vapor.

TABLE VIII.—DENSITIES OF NH_4Br VAPOR (SATURATED)—SUMMARY.

| | | Vapor Density. | | | | | Pressure. Total mm. |
|-------|------|----------------|-----------------------------|--|--|------------------------------|---------------------------|
| Temp. | | Observed. | | Calculated. | | | |
| C. | Abs. | G. per cc. | Mols per l. Δm . | Interpol. Mols per l. Δm_i . | Undissoc. Mols per l. δm . | Comp. dissoc. Mols per l. | |
| 300 | 573 | 0.000130 | 0.00133 | 0.00104 | 0.00154 | 0.00077 | 55.0 |
| 310 | 583 | | | 0.00143 | 0.00205 | 0.00103 | 74.6 |
| 320 | 593 | 0.000192 | 0.00196 | 0.00195 | 0.00272 | 0.00136 | 100.6 |
| 330 | 603 | 0.000259 | 0.00264 | 0.00266 | 0.00358 | 0.00179 | 134.7 |
| 340 | 613 | 0.000348 | 0.00356 | 0.00358 | 0.00468 | 0.00234 | 178.8 |
| 350 | 623 | 0.000478 | 0.00488 | 0.00482 | 0.00609 | 0.00305 | 236.6 |
| 360 | 633 | 0.000633 | 0.00646 | 0.00645 | 0.00786 | 0.00393 | 310.4 |
| 370 | 643 | 0.000836 | 0.00853 | 0.00858 | 0.01010 | 0.00505 | 404.8 |
| 380 | 653 | 0.00110 | 0.0112 | 0.0114 | 0.01290 | 0.00645 | 525.5 |
| 388 | 661 | 0.00142 | 0.0145 | 0.0142 | 0.01564 | 0.00782 | 644.4 |

The Degrees of Dissociation.—The degrees of dissociation of ammonium bromide vapor are calculated by the same method as were those of ammonium chloride. The results are presented in Table IX and are plotted in Fig. 3. The quantities in the several columns of Table IX have the same significance as those in the corresponding columns of Table IV (ammonium chloride).

TABLE IX.— NH_4Br —DEGREES OF DISSOCIATION.

| Temp. C. | Percentage dissociation. | | Deviation of α from straight line. | | % error in α . (Calcd.) |
|-------------|--------------------------|-----------|--|-----|-----------------------------------|
| | Obsd. | Interpol. | Actual. | %. | |
| 300° | 16.1 | 47.9 | —31.8 | .. | .. |
| 310° | .. | 43.6 | .. | .. | .. |
| 320° | 38.7 | 39.3 | —0.6 | 1.5 | 4.3 |
| 330° | 35.7 | 34.9 | +0.8 | 2.3 | 9.8 |
| 340° | 31.6 | 30.6 | +1.0 | 3.3 | 7.1 |
| 350° | 24.7 | 26.3 | —1.6 | 6.1 | 6.5 |
| 360° | 21.7 | 22.0 | —0.3 | 1.4 | 5.4 |
| 370° | 18.4 | 17.7 | +0.7 | 4.0 | 3.7 |
| 380° | 15.3 | 13.4 | +1.9 | 14 | 18 |
| 388° | 8.0 | 10.0 | —2.0 | 20 | 12 |

Inspection of Table IX and of Fig. 3 will show that at 320° ammonium bromide vapor is about 39% dissociated and, as the temperature increases, the degree of dissociation *decreases* regularly until at 388° it is only about 8–10%. As was the case with ammonium chloride, a straight line represents the results within the experimental error of the observations.

As will be seen from Table IX, the deviations of the measured values of α from a straight line are, with one or two exceptions, less than the deviations calculated from the known experimental error in the observed vapor densities.

The exact degree of dissociation at temperatures below 320° is somewhat in doubt. If, below 320° , the degree of dissociation continued to vary linearly with the temperature, as it does above 320° , it should have a value of about 48% at 300° , with a corresponding vapor density of 0.000102 g. per cc. We first used bulbs of type No. 2 (Fig. 1), and obtained a set of nine densities with the average value $0.000135 \pm 3.1\%$ (not given in the table), corresponding to a dissociation of 11.1%. Later, we repeated the determination using the trap bulb, No. 3 (Fig. 1), and obtained the value cited above, namely 0.000130 g. per cc. (16.1% dissociation).¹ The mean of the two values 0.0001325, differs from each of the values by less than 2%. Since at this temperature the vapor pressure is very low, the total weight of the vapor filling the large bulb is only 8-10 mg. The agreement of the two sets within 4% is therefore better than one would expect under the conditions. On the other hand, it seems improbable that the real value was 0.000102, and that the errors in the two sets were as great as 25% and 30%, respectively. Speaking conservatively, all that can be said is, that the measurements indicate that the degree of dissociation of ammonium bromide vapor passes through a maximum near 320° , but that this inference depends entirely upon the vapor density at 300° , which is the one most subject to error in the series.

As already pointed out, the measurements are not made at constant pressure, but at pressures which rise rapidly with rising temperature. Thus between 330° and 380° the total pressure of all components increases from 134.7 mm. to 644.4 mm., while the partial pressure of free ammonia (or HBr, see Table XV) increases from 34.6 mm. to 57.8 mm. only. Calculation shows that if the total pressure were to be kept constant at 134.7 mm. then the partial pressure of ammonia would change from 34.6 mm. to 23.5 mm. Hence, the degree of dissociation would decrease from 35% to 21% only. Thus the decrease shown in Table IX is greatly exaggerated by the effect of increasing total pressure. Ammonium bromide vapor is apparently the only dissociating gas whose degree of dissociation at constant pressure is known to decrease with increasing temperature.

In this connection attention should be called to the fact that this behavior is not unique, in the sense that many, and therefore possibly all

¹ This case illustrates very strikingly the way in which a moderate error in the observed density gives rise to a very large error in the degree of dissociation calculated therefrom. Here the higher of the two values obtained for the density exceeded the lower by 4%, while one of the corresponding, calculated values of α is no less than 45% greater than the other (see p. 49).

other substances are *known* to show the opposite behavior. If this were true, the isolated nature of the phenomenon would enjoin extreme caution before acceptance. The situation is, rather, that we lack information in regard to almost all the other dissociating substances, and do not know what their behavior in this respect is. For example, the vapor density of ammonium bromide was previously investigated by Deville and Troost by the Dumas method, and the results did give a slightly greater (2%) density (and therefore less dissociation) at the higher temperature (Table I). But this difference was quite naturally attributed to error, due to the inadequacy of the method when applied to such substances. The data thus far obtained in regard to the vapor densities of solids dissociating at high temperatures simply have not usually been such as would enable us to distinguish with certainty between cases in which, with rising temperature, the dissociation increased, and those in which it decreased.

The Latent Heat of Vaporization.—The only previous attempt to determine the molar latent heat of vaporization of ammonium bromide is that of F. M. G. Johnson,¹ who, by using the equation $d \ln P/dT = Q/2RT^2$, in conjunction with his measurements of the vapor pressures of ammonium bromide, found the value 45.4 kg. cal. at 297–394°. Since this equation involves the assumption that ammonium bromide vapor is completely dissociated, Johnson's value is larger than the correct value, and does not represent the heat absorbed when one mol of ammonium bromide vaporizes in equilibrium with its saturated vapor.

We have calculated the molar latent heat of vaporization from the following equation, which was derived and explained when the latent heat of vaporization of ammonium chloride was discussed, namely,

$$L = T_{760} \left[\frac{A}{0.4343 T^2} + \frac{B}{T} \right] \frac{0.02419}{\Delta_{mi}} \text{ kg. cal.}$$

For ammonium bromide, $A = 2057$, and $B = 9.540$.²

The values of the latent heat of vaporization thus obtained are given in Table X.

TABLE X.—NH₄Br—LATENT HEATS OF VAPORIZATION (Kg. cal. per mol).

| 300° | 320° | 330° | 340° | 350° | 360° | 370° | 380° | 388° |
|------|------|------|------|------|------|------|------|------|
| 23.5 | 28.7 | 28.1 | 27.4 | 26.8 | 26.1 | 25.4 | 24.7 | 24.1 |

These values of the latent heat of vaporization are less than those of Johnson, as would be expected from the nature of the error in his determinations. The fact that above 320° the latent heat of vaporization decreases is not unusual. If the vapor of a solid or a liquid does not dissociate, the latent heat of vaporization will, in general, decrease with increasing temperature, because the specific heat of the solid or liquid is greater than that of its

¹ F. M. G. Johnson, *Z. physik. Chem.*, 65, 38 (1908–9).

² Smith and Calvert, *THIS JOURNAL*, 36, 1368 (1914).

saturated vapor. Ammonium bromide, therefore, behaves in this respect exactly like a normal, nondissociated substance. It must consequently be concluded that the disturbing influences upon the heat of vaporization (*e. g.*, the heat involved in the dissociation of the vapor) are insufficient to affect the general run of the results, or are approximately constant throughout the temperature range considered.

The Dissociation Constants and the Heat of Dissociation.—The dissociation constants of ammonium bromide vapor were calculated from the data in Table VIII by the same relation which was used in the case of ammonium chloride, namely,

$$K_c = \frac{\alpha^2}{1 - \alpha} \Delta_{mi}.$$

As under ammonium chloride, two series of values of K_c were determined, one by using the observed values of α and the second by using the "interpolated" values of α . The latter series represents the best average of the measured dissociation constants. These observed and "average"

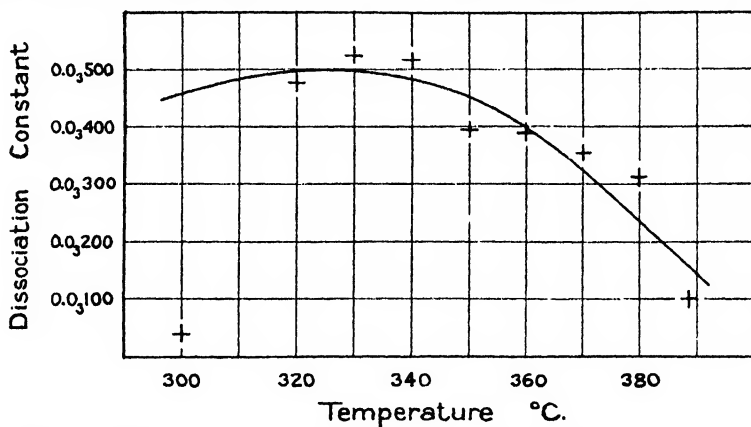


Fig. 7.—Dissociation constants of saturated ammonium bromide vapor.

dissociation constants are given in Table XI; and they are plotted in Fig. 7. The "average" values are represented by the curve, and the observed values by the points which lie on either side of the curve.

TABLE XI.— NH_4Br —DISSOCIATION CONSTANT, K_c .

| Temp. | Observed. | Average. | Temp. | Observed. | Average. |
|-------|-----------|----------|-------|-----------|----------|
| 300° | 0.03409 | 0.03458 | 350° | 0.03396 | 0.03453 |
| 310° | 0.03481 | 0.03481 | 360° | 0.03390 | 0.03400 |
| 320° | 0.03478 | 0.03497 | 370° | 0.03353 | 0.03327 |
| 330° | 0.03525 | 0.03497 | 380° | 0.03311 | 0.03236 |
| 340° | 0.03517 | 0.03483 | 388° | 0.03198 | 0.03158 |

It will be seen that the dissociation constant first increases to a maximum at 320°, and then decreases. If we consider first the decrease, we see that this has an important bearing upon the heat of dissociation. If

in the van't Hoff equation, $d \ln K_c/dT = -U/RT^2$, the term $d \ln K_c/dT$ is negative, as it is here above 320° , then U must be *positive*. That is to say, above 320° , heat will be *evolved* by the reaction. Hence, the data show that above 320° the dissociation of ammonium bromide vapor is accompanied by evolution of heat. This result was wholly unexpected. If the decrease had been slight, it might have been explained as due to errors of observations, or to inadequacy of the method, for the measurement of vapor densities at high temperatures is undoubtedly difficult and subject to considerable errors. The decrease is so very rapid, however; the values at the various temperatures are so regular in their decrease, and the estimated errors of observation are relatively so small (see Table VII), that no doubt can exist that the decrease really occurs.

As regards the maximum point, the phenomena are the opposite of those shown by hydrogen iodide, where at low temperatures heat is given out in the dissociation and at higher temperatures is absorbed, so that the dissociation constant passes through a minimum. The cases are not parallel, however, because the decomposition of the hydrogen iodide is accompanied by recombination to form HI_2 and I_2 , and the case is not one of simple dissociation like that of ammonium bromide. Although the case of ammonium bromide is thus unique among gases, there are analogies among liquids which, to a certain extent, reconcile us to its occurrence. Thus, Lundén¹ has found that with rising temperature the ionic dissociation constants of ammonium hydroxide and of acetic acid pass through maxima. However, the case is not strictly analogous, because the conditions in a system involving two components, such as a solution, are different from those in a system involving only one component like the present one. The analogy is closer in a single ionizing liquid like water. According to Arrhenius' equation $U = A_0 - CT^2$, U being here the heat of ionic dissociation, there must be for each substance some temperature at which the dissociation reaches a maximum. This happens when $U = 0$, and therefore $T = \sqrt{A_0/C}$. In the case of water this temperature happens to fall within the experimental range. According to A. A. Noyes² $U = 0$ for water between 250° and 275° . According to Arrhenius³ $U = 0$ for water at 229° . It is therefore quite conceivable that similar relations should exist in dissociating vapors.

An attempt to obtain an expression for the values of the heat of dissociation of ammonium bromide by means of the combined van't Hoff and Arrhenius equations, which served so well in the case of ammonium chloride, was made. It was found, however, that for ammonium bromide this equation does not represent the relation between the dissociation

¹ Lundén, *J. chim. phys.*, **5**, 598 (1907).

² Carnegie Inst. of Washington, Publication No. 63, 233 (1907).

³ "Theories of Solutions" 1912, p. 212.

constants and the heat of dissociation. Arrhenius himself found that his interpolation formula does not always apply where a change in the sign of U occurs. In such cases it can be used with success only where the sign of U passes through zero at a moderate temperature. For example, it does not represent the heat of electrolytic dissociation of water at temperatures much above the boiling point of water, unless powers of T higher than the second are included. Since, in the present instance, the change in sign occurs as high as 320° , the Arrhenius formula could not be expected to hold.

Ammonium Iodide.

The Data.—The densities of saturated ammonium iodide vapor were determined from 300° to 380° by using the "trap" bulb, Fig. 1, No. 3. The bulbs remained in the nitrate bath for thirty minutes each. Ammonium iodide, once recrystallized, and dried at 100° *in vacuo*, was used. The vapor density data are presented in Table XII.

TABLE XII.—DENSITIES OF NH_4I VAPOR (SATURATED)—DATA.

| Temp. | G. NH_4I in large bulb. | Vol. (cc.) of large bulb. | Vapor dens. g. per cc. | Deviation from mean. |
|----------------------------|---|---------------------------|------------------------|---------------------------|
| 300° | 0.0158 | 77.88 | 0.000203 | + 22 |
| | 0.0144 | 75.42 | 0.000191 | + 10 |
| | 0.0114 | 74.35 | 0.000153 | — 28 |
| | 0.0073 | 68.74 | 0.000106 | ... |
| | 0.0108 | 63.94 | 0.000169 | — 12 |
| | 0.0137 | 73.02 | 0.000188 | + 7 |
| Average vapor density..... | | | 0.000181 | ± 7 , or $\pm 3.9\%$ |
| 320° | 0.0233 | 73.94 | 0.000315 | + 8 |
| | 0.0227 | 73.93 | 0.000307 | 0 |
| | 0.0232 | 77.07 | 0.000301 | — 6 |
| | 0.0262 | 81.45 | 0.000322 | + 15 |
| | 0.0201 | 65.78 | 0.000306 | — 1 |
| | 0.0213 | 73.28 | 0.000291 | — 16 |
| Average vapor density..... | | | 0.000307 | ± 3 , or $\pm 1.0\%$ |
| 340° | 0.0233 | 76.65 | 0.000304 | ... |
| | 0.0367 | 68.72 | 0.000534 | + 46 |
| | 0.0425 | 78.24 | 0.000543 | + 55 |
| | 0.0330 | 68.64 | 0.000481 | — 7 |
| | 0.0278 | 70.52 | 0.000394 | — 94 |
| | 0.0390 | 71.86 | 0.000543 | + 55 |
| | 0.0280 | 75.77 | 0.000370 | — 118 |
| | 0.0367 | 67.58 | 0.000543 | + 55 |
| | 0.0358 | 66.05 | 0.000542 | + 54 |
| | 0.0360 | 80.25 | 0.000443 | — 45 |
| Average vapor density..... | | | 0.000488 | ± 19 , or $\pm 3.9\%$ |
| 350° | 0.0491 | 72.96 | 0.000673 | + 26 |
| | 0.0470 | 70.24 | 0.000669 | + 22 |
| | 0.0450 | 67.50 | 0.000667 | + 20 |
| | 0.0437 | 74.56 | 0.000579 | — 68 |
| Average vapor density..... | | | 0.000647 | ± 17 , or $\pm 2.6\%$ |

TABLE XII.—DENSITIES OF NH_4I VAPOR (SATURATED)—DATA (*continued*).

| Temp. | G. NH_4I in large bulb. | Vol. (cc.) of large bulb. | Vapor dens. g. per cc. | Deviation from mean. |
|----------------------------|---|---------------------------|------------------------|---------------------------|
| 360° | 0.0687 | 82.41 | 0.000834 | — 40 |
| | 0.0743 | 86.80 | 0.000856 | — 18 |
| | 0.0699 | 78.67 | 0.000889 | + 15 |
| | 0.0768 | 89.39 | 0.000859 | — 15 |
| | 0.0749 | 82.76 | 0.000905 | — 31 |
| | 0.0637 | 69.56 | 0.000903 | + 29 |
| Average vapor density..... | | | 0.000874 | ± 10 , or $\pm 1.1\%$ |
| 370° | 0.0755 | 68.83 | 0.00110 | + 5 |
| | 0.0722 | 69.14 | 0.00104 | — 1 |
| | 0.0740 | 72.53 | 0.00102 | — 3 |
| | 0.0696 | 69.02 | 0.00101 | — 4 |
| | 0.0682 | 66.25 | 0.00103 | — 2 |
| | 0.0759 | 71.32 | 0.00108 | — 3 |
| Average vapor density..... | | | 0.00105 | ± 1 , or $\pm 1.0\%$ |
| 380° | 0.0947 | 74.92 | 0.00126 | — 3 |
| | 0.1001 | 79.49 | 0.00126 | — 3 |
| | 0.1004 | 78.96 | 0.00127 | — 2 |
| | 0.1062 | 86.88 | 0.00120 | — 9 |
| | 0.1088 | 75.22 | 0.00143 | + 14 |
| Average vapor density..... | | | 0.00129 | ± 3 , or $\pm 2.3\%$ |

The error in the ammonium iodide vapor densities is, at several of the temperatures, greater than that observed for the chloride and bromide; and the average values of the vapor densities do not lie so smoothly on a curve. This greater irregularity may be due to the slow decomposition of the hydrogen iodide,¹ although no iodine vapor was ever noticed in the hot vapor density bulbs immediately after they were removed from the nitrate bath (see also p. 67).

TABLE XIII.—DENSITIES OF NH_4I VAPOR (SATURATED)—SUMMARY.

| Temp. | | Vapor density. | | | | | Pressure. Total. mm. |
|-------|------|----------------|-----------------------------|--|--|----------------------------------|----------------------------|
| | | Observed. | | Calculated. | | | |
| | | G. per cc. | Mols per l. Δm . | Interpol. Mols per l. Δm_i . | Undissoc. Mols per l. δm . | Compl. dissoc. Mols per l. | |
| C. | Abs. | | | | | | |
| 300 | 573 | 0.000181 | 0.00125 | 0.00126 | 0.00095 | 0.00048 | 33.9 |
| 310 | 583 | | ... | 0.00166 | 0.00133 | 0.00067 | 48.5 |
| 320 | 593 | 0.000307 | 0.00212 | 0.00212 | 0.00185 | 0.00093 | 68.4 |
| 330 | 603 | | ... | 0.00270 | 0.00253 | 0.00126 | 95.0 |
| 340 | 613 | 0.000488 | 0.00337 | 0.00345 | 0.00341 | 0.00170 | 130.3 |
| 350 | 623 | 0.000647 | 0.00446 | 0.00447 | 0.00454 | 0.00227 | 176.3 |
| 360 | 633 | 0.000874 | 0.00603 | 0.00573 | 0.00597 | 0.00299 | 235.7 |
| 370 | 643 | 0.00105 | 0.00721 | 0.00730 | 0.00777 | 0.00389 | 311.5 |
| 380 | 653 | 0.00129 | 0.00886 | 0.00898 | 0.0100 | 0.00500 | 407.3 |

The vapor density results are summarized in Table XIII, as was done in Table III for ammonium chloride. The dissociation pressures given

¹ Smith and Calvert, *THIS JOURNAL*, 36, 1370 (1914).

in this table are those of Smith and Calvert.¹ The "interpolated" values of the vapor density given in Table XIII were not determined by calculation from the interpolated values of α , as in the case of ammonium chloride, because, as will be seen below, the values of α for ammonium iodide cannot be determined. The "interpolated" values were therefore found by graphical interpolation from the best representative curve which could be drawn through the observed vapor densities. This curve, together with the "undissociated" and "completely dissociated" vapor density curves are given in Fig. 8.

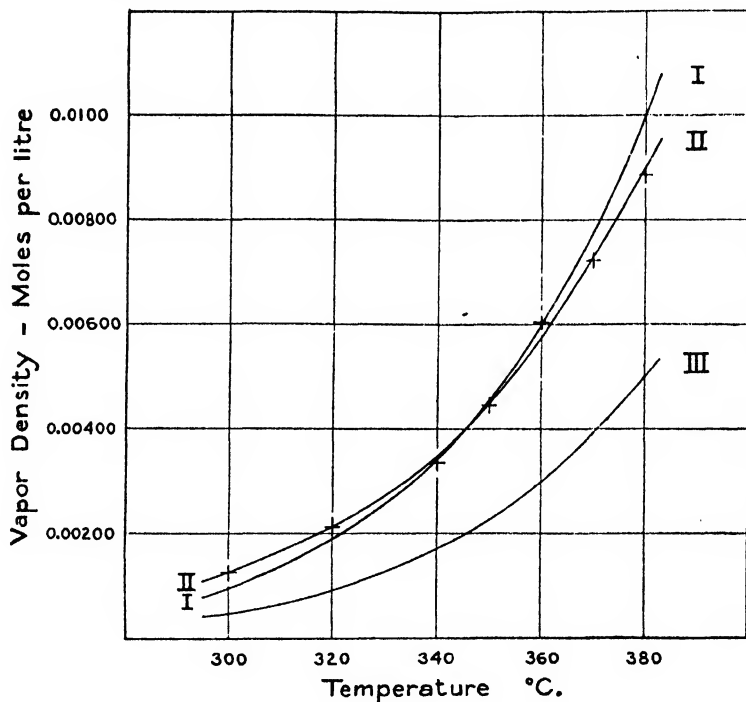


Fig. 8.—Vapor densities of ammonium iodide: Curve I—Undissociated (calculated); Curve II—Observed; Curve III—Completely dissociated (calculated).

Discussion of Results.—Inspection of Table XIII and of Fig. 8 shows several interesting facts concerning ammonium iodide vapor. It will be noticed that, below 340–350°, the observed densities of the saturated vapor are larger than the densities calculated for no dissociation. This means that ammonium iodide vapor is associated. However, it does not exclude the possibility that part of the vapor is also dissociated at the same time, although it does indicate that the amount of association at lower temperatures is relatively larger than the amount of dissociation. The

¹ Smith and Calvert, *Loc. cit.*, 1371.

equilibrium in the vapor at any temperature may be represented most simply by the equation,



It will be seen also that, as the temperature increases, the observed vapor densities become first equal to, and then less than the "undissociated" vapor densities. This indicates that the amount of association decreases and the amount of dissociation increases as the temperature of the vapor rises.

The unexpected character of the results suggests the possibility of some secondary reaction. Thus, if the hydrogen iodide itself dissociated, the free iodine might interact with the ammonia to produce free nitrogen and hydrogen iodide. This reaction would result in a diminished partial pressure of ammonia, which in turn would permit further vaporization of the salt, and so give greater apparent densities. A similar reaction might even be imagined to have occurred in the case of the bromide. Such a reaction, however, would have left permanent gases (nitrogen and hydrogen) in the bulb. Now, in all the measurements in this paper, the evacuated bulbs, when opened under water, were filled completely by the liquid. The minute bubble of gas (much less than 1 cc.) which was visible, appeared to come mainly from the atmospheric gases dissolved in the water. Hence no reaction producing a permanent gas can have occurred.

The association of ammonium iodide vapor renders it impossible to make for it many of the calculations which were made for ammonium chloride and bromide. If it is assumed that the equilibrium in the vapor is represented by Equation I above, and if α is the percentage of the total number of NH_4I molecules dissociated, and β the percentage associated at any temperature, then

$$(\alpha - 0.5 \beta) = \frac{\delta_m - \Delta_m}{\Delta_m}. \quad (\text{II})$$

This is the only relation between α and β which can be obtained from our data, and therefore, since there is only one equation involving these two unknown quantities, it is impossible to determine either of them. Since α and β are indeterminable, the dissociation constants, the heat of dissociation, and the partial pressures cannot be calculated, because the values of α and β are necessary for the calculation of each of these.

Although it is thus impossible to determine the actual degree of association or of dissociation of the vapor, the maximum and minimum values at any temperature may be estimated. At temperatures below that at which the observed and the "undissociated" vapor density curves cross each other, the minimum value of β may be found by placing α in Equation II equal to zero, and solving for β . The minimum value of α in this temperature region is, of course, zero. At temperatures above the inter-

section of these two curves, the minimum value of β is zero, and the minimum value of α may be found by assuming β in Equation II to be zero, and solving for α . The maximum values of α and β may be determined by assuming that all of the NH_4I molecules in the vapor have associated and dissociated; *i. e.*, by assuming that $\alpha + \beta = 1.00$, and then solving the simultaneous equations

$$\begin{aligned}\alpha - 0.5\beta &= \frac{\delta_m - \Delta_m}{\Delta_m} \\ \alpha + \beta &= 1.00\end{aligned}$$

In this way we have estimated that ammonium iodide vapor at 300° is between 24% and 83% associated, and from 0% to 17% dissociated. At 380° , it is between 0% and 59% associated, and from 11% to 41% dissociated. These estimates are, of course, based upon the assumption that there are no ammonium iodide molecules in the vapor more complex than the type $(\text{NH}_4\text{I})_2$, but they give some idea as to the conditions possibly present.

The Latent Heat of Vaporization.—F. M. G. Johnson¹ has found the value 44.5 kg. cal. for the molar latent heat of vaporization of ammonium iodide by the same method which he used for the chloride and bromide. But this method involves the assumption of the complete dissociation of the vapor, and so his result is too large. This is apparently the only estimate of the latent heat of vaporization of ammonium iodide which has thus far been made.

We have computed the molar latent heat of vaporization from the data in Table XIII, by the method we used for ammonium chloride and bromide, the equation for ammonium iodide being

$$L = T \frac{P}{760} \left[\frac{7715}{0.4343 T^2} - \frac{10.04}{T} \right] \frac{0.02419}{\Delta_{mi}} \text{ kg. cal.}$$

The values obtained are given in Table XIV. Those at 310° and 330° are in italics because they were calculated from purely interpolated data, there being no measured vapor densities of ammonium iodide at these temperatures. In the last line of the table are given the differences between the successive values of the heat of vaporization, in order that its mode of variation with the temperature may be clearly seen.

TABLE XIV.— NH_4I —LATENT HEATS OF VAPORIZATION (Kg. cal. per mol).

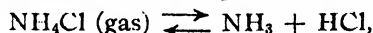
| 300° | 310° | 320° | 330° | 340° | 350° | 360° | 370° | 380° |
|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 18.0 | <i>19.0</i> | 20.4 | <i>21.7</i> | 22.8 | 23.2 | 23.6 | 23.9 | 24.8 |
| | 1.0 | 1.4 | 1.3 | 1.1 | 0.4 | 0.3 | 0.3 | 0.9 |

The latent heat of vaporization of ammonium iodide increases as the temperature increases. Since the latent heat of vaporization of substances whose vapors are neither associated or dissociated generally

¹ F. M. G. Johnson, *Z. physik. Chem.*, **65**, 40 (1908-9).

decreases with a rise of temperature, the above fact makes it probable that heat is absorbed during the dissociation of ammonium iodide vapor, and that the amount of heat absorbed by dissociation increases as the temperature increases. This latter fact would be expected, because it has already been shown that the amount of dissociation of ammonium iodide vapor increases as the temperature rises.

The Partial Pressures of the Ammonium Halides.—The partial pressures for ammonium iodide could not be calculated on account of the association of its vapor. Taking ammonium chloride as an example, and assuming the equilibrium in the vapor to be of the type,



the partial pressures of the three gases in the vapor are given by the formulae

$$p_{\text{NH}_4\text{Cl}} = P_{\text{Total}} \frac{2\Delta_{mi} - \delta_m}{\delta_m}, \text{ and } p_{\text{NH}_3} = p_{\text{HCl}} = \frac{P_{\text{Total}} - p_{\text{NH}_4\text{Cl}}}{2}.$$

P_{Total} is the dissociation pressure of the ammonium halide in question. The data for ammonium chloride and bromide, given in Tables III and VIII, respectively, were used for calculating the partial pressures, and the results are presented in Table XV.¹

TABLE XV.— NH_4Cl AND NH_4Br —PARTIAL PRESSURES.

| Temp. C. | Ammonium chloride. | | | Ammonium bromide. | | |
|-------------|---------------------------|-----------------------------------|---|---------------------------|-----------------------------------|---|
| | P_{Total} Mm. | $p_{\text{NH}_4\text{Cl}}$ Mm. | $p_{\text{NH}_3} = p_{\text{HCl}}$ Mm. | P_{Total} Mm. | $p_{\text{NH}_4\text{Br}}$ Mm. | $p_{\text{NH}_3} = p_{\text{HBr}}$ Mm. |
| 280° | 135.0 | 30.3 | 52.4 | ... | ... | .. |
| 290° | 185.3 | 37.9 | 73.7 | ... | ... | .. |
| 300° | 252.5 | 53.2 | 99.7 | 55.0 | 19.3 | 17.9 |
| 310° | 341.3 | 73.8 | 133.8 | 74.6 | 29.5 | 22.6 |
| 320° | 458.1 | 101.2 | 178.5 | 100.6 | 43.6 | 28.5 |
| 330° | 610.6 | 141.7 | 234.5 | 134.7 | 65.5 | 34.6 |
| 340° | ... | ... | ... | 178.8 | 94.8 | 42.0 |
| 350° | ... | ... | ... | 236.6 | 137.9 | 49.4 |
| 360° | ... | ... | ... | 310.4 | 199.0 | 55.7 |
| 370° | ... | ... | ... | 404.8 | 282.9 | 61.0 |
| 380° | ... | ... | ... | 525.5 | 403.3 | 61.1 |
| 388° | ... | ... | ... | 644.4 | 528.8 | 57.8 |

Summary.

Measurements of the densities of the saturated vapors of ammonium chloride (280° to 330°), bromide (300° to 388°), and iodide (300 to 380°) are recorded. With these data, and the previously measured dissociation pressures, a study is made of the degrees of dissociation, dissociation constants, heats of dissociation, latent heats of vaporization, and partial pressures of these substances, with the following results:

¹ In order to facilitate reference and comparison, we have also given in Table XV the dissociation pressures of ammonium chloride and bromide as measured by Smith and Calvert (*Loc. cit.*).

Ammonium chloride vapor is 67-63% dissociated between 280° and 330°; and although the degree of dissociation is very nearly constant, it decreases slightly between these temperatures. Ammonium bromide vapor is about 39% dissociated at 320°, and above this temperature the percentage dissociation decreases linearly, until, at 388°, it is about 10%. Ammonium iodide vapor is associated, especially at lower temperatures, but the amount of association decreases, and the dissociation increases as the temperature rises. The assumption that the vapors of the ammonium halides are completely dissociated is therefore no longer tenable.

The dissociation constants of ammonium chloride and bromide are calculated. That of ammonium chloride vapor increases steadily with the temperature, whereas that of ammonium bromide vapor passes through a maximum near 320°, and then decreases.

The heat of dissociation of ammonium chloride vapor is computed by the van't Hoff equation, and is represented by the relation, $U = -12800 - 0.00967T^2$ gram calories (U is heat evolved). The mode of variation of the dissociation constant with the temperature indicates that the dissociation of ammonium bromide vapor above 320° is accompanied by the evolution of heat, but the actual value of the heat of dissociation can not be computed.

The latent heats of vaporization are calculated by the Clausius-Clapeyron equation. That of ammonium chloride is 32.9 kg. cal. between 280° and 330°, and is constant within 1%; that of ammonium bromide is 28.7 kg. cal. at 320°, and decreases to 24.1 at 388°; that of ammonium iodide increases from 18.0 kg. cal., at 300°, to 24.2 at 380°.

The partial pressures of the various components in the ammonium chloride and bromide vapors are computed.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK, N. Y.

ON THE RATE OF REDUCTION OF MERCURIC CHLORIDE BY SODIUM FORMATE.

By G. A. LINHART.

Received November 12, 1914.

In a previous paper¹ an investigation of the rate of the reduction of mercuric chloride by phosphorous acid was described. The purpose of this article is to present the results of a similar study of the rate of reduction of mercuric chloride by sodium formate, with special reference to the influence of sodium chloride upon it, which has already been shown to have a great effect on the reduction by phosphorous acid.

Very recently, after the experimental work described below had been

¹ Linhart, *Am. J. Sci.*, **35**, 353-368 (1913).

completed, a preliminary communication on this same subject was published by Findlay and Davies.¹ These investigators conclude from a large number of experiments at various temperatures and concentrations that the reaction between sodium formate and mercuric chloride is one of the second order, because when their experimental results are substituted in an equation representing a reaction of the third order the reaction velocity coefficient gradually increases to about 40%, while if substituted in one representing a reaction of the second order, the velocity coefficient decreases only by about 17%. As these figures created some doubt, in the authors' own minds as to the mechanism of this reaction, they cited the similar reaction between mercuric chloride and phosphorous acid,² which has been shown to be of the second order, and state that a similar explanation to justify the assumption that the reaction between mercuric chloride and sodium formate is theoretically one of the second order, appears to be very doubtful. It will be evident from what follows, not only that the mechanism of the reaction between mercuric chloride and sodium formate may be interpreted in a similar manner to that of mercuric chloride and phosphorous acid, but that concordant velocity constants may be obtained if the experiments are performed under the proper conditions.

There are two opposing factors which tend to obscure the mechanism of the reaction between mercuric chloride and sodium formate. First, the association of the mercuric chloride in water solution;³ and secondly, the formation of sodium chloride. The double molecules of mercuric chloride being present in considerable proportion at higher temperatures and gradually dissociating with the dilution would tend to accelerate the velocity of the reaction to some extent, as the simple molecules are found to be more reactive. On the other hand, the sodium chloride, increasing in concentration as the reaction proceeds, combines with the mercuric chloride, forming NaHgCl_2 , and subsequently Na_2HgCl_4 , which react with the sodium formate extremely slowly, as is shown in the table, Expt. 7. Since the second factor very much more than compensates the first, the velocity coefficient, K , will consequently decrease. In order to overcome these difficulties the reaction must be allowed to take place either at such dilutions that the mercuric chloride is practically all in the form of simple molecules, HgCl_2 , so that the resulting sodium chloride can exert no appreciable influence; or, in a large excess of sodium chloride so that there could be no free HgCl_2 molecules, and the influence of the small amount of sodium chloride, formed in the course of the reaction, would

¹ *J. Chem. Soc.*, 103, 1550-1554 (1913).

² See discussion of results.

³ A paper on this subject is ready for publication. See also Sand and Breest, *Z. physik. Chem.*, 59, 426; 60, 237; Jander, *Z. Electrochem.*, 8, 688.

be negligible as compared with the total amount initially present. There is another factor which tends to modify the course of the reaction, namely, the formation of hydrochloric acid, but this may easily be remedied either by the addition to the reaction mixture of a soluble salt of a weak acid, as was recommended in a previous paper,¹ or by the addition of a sufficient amount of finely divided barium carbonate.

Experimental.

Standardization of the Mercuric Chloride and Sodium Formate.—A weighed amount of mercuric chloride was dissolved in distilled water or in aqueous sodium chloride of known concentration. Of this solution 10 cc. were pipeted off, by means of a carefully calibrated pipet, and transferred into several glass test tubes, of about 40 cc. capacity, which had previously been constricted at about $1\frac{1}{2}$ " from the mouth to a size just large enough to admit the stem of the pipet and to allow the displaced air to escape. To this were added 10 cc. of a solution containing about twice the theoretical amount of sodium formate. The tubes were then sealed, allowed to cool, the contents well mixed, and the tubes submerged in a thermostat kept at 40° . When two consecutive analyses of the mercurous chloride in the tubes about twenty-four hours apart showed no increase in the amount of the mercurous chloride, the reduction was considered complete. Moreover, these results always agreed within 0.2-0.3%, with the theoretical amount of mercurous chloride calculated from the mercuric chloride originally present. In a similar manner the concentration of the sodium formate was determined by using an excess of mercuric chloride.

Reaction Velocity Measurements.—All experiments were carried out in sealed glass test tubes. As soon as two tubes were filled with 10 cc. of the standardized mercuric chloride containing the sodium chloride, and 10 cc. of the standardized sodium formate, containing the sodium acetate, they were sealed, allowed to cool, shaken and submerged in a thermostat kept at 40° , where they were held in position by means of coiled brass springs. The time, t , was counted from the moment the tube was submerged until it was removed from the thermostat and plunged into ice water to check the reaction. At definite intervals a tube was withdrawn; the capillary tip carefully broken off and three scratches made with a sharp triangular file in a horizontal plane, on each side of which was placed a folded piece of wet filter paper. The tube was then brought in a vertical position at the point of a small blast lamp flame, care being taken not to allow the upper part of the tube to fly off, as it often contained some

¹ Linhart, *New York Med. J.*, June 14, 1913. The addition of sodium acetate, sodium citrate, and sodium bicarbonate, in particular, causes the reaction between mercuric chloride and phosphorous acid to become instantaneous, while in the case of mercuric chloride and sodium formate the action is merely accelerated.

mercurous chloride. After the tube was thus cracked the upper part was lifted off and the contents filtered through an ignited and weighed perforated platinum crucible, fitted with an asbestos mat. The precipitate was washed first with warm water, then with a little dilute hydrochloric acid, and finally with warm water until the wash water was free of impurities. It was found advisable in filtering the mercurous chloride to use light suction at first to avoid clogging of the asbestos mat, which would vitiate the experiment because of the delay in stopping the reaction. After most of the moisture had been exhausted by the aspirator, the crucible was suspended in a drying oven maintained at a temperature between 105° and 110° for thirty minutes. The crucible was then allowed to cool in a desiccator and weighed.

TABLE I.

Experimental Results at 40° Showing the Retarding Influence of Sodium Chloride.

| Expt. No. | Initial concn. | t in hours. | HgCl in grams. | x in mols. | K. |
|-----------|----------------|-------------|----------------|------------|-------|
| 1..... | A = 0.01 | 3.1 | 0.0135 | 0.002866 | 1.80 |
| | B = 0.061 | 4.6 | 0.0182 | 0.003864 | 1.79 |
| | (NaAc = 0.5) | 8.6 | 0.0282 | 0.005987 | 1.79 |
| | (NaCl = 0.0) | 18.8 | 0.0404 | 0.008578 | 1.78 |
| | | 23.7 | 0.0431 | 0.009151 | 1.80 |
| | | ... | 0.0471 | 0.010000 | ... |
| 2..... | A = 0.01 | 36.5 | 0.0135 | 0.002866 | 1.74 |
| | B = 0.0061 | 83.0 | 0.0231 | 0.004904 | 1.75 |
| | (NaAc = 0.5) | 106.0 | 0.0262 | 0.005563 | 1.75 |
| | (NaCl = 0.0) | 205.0 | 0.0345 | 0.007325 | 1.77 |
| | | 318.0 | 0.0388 | 0.008238 | 1.75 |
| | | 560.0 | 0.0431 | 0.009149 | 1.75 |
| | | ... | 0.0471 | 0.010000 | ... |
| 3..... | A = 0.1 | 1.9 | 0.0685 | 0.01454 | 1.43 |
| | B = 0.061 | 5.7 | 0.1528 | 0.03244 | 1.32 |
| | (NaAc = 0.5) | 8.4 | 0.1930 | 0.04098 | 1.27 |
| | (NaCl = 0.0) | 18.1 | 0.2797 | 0.05938 | 1.17 |
| | | 29.0 | 0.3340 | 0.07091 | 1.14 |
| | | 44.8 | 0.3772 | 0.08008 | 1.10 |
| | | 55.0 | 0.3946 | 0.08378 | 1.09 |
| | | 76.5 | 0.4196 | 0.08909 | 1.07 |
| | | ... | 0.4710 | 0.10000 | ... |
| 4..... | A = 0.1 | 2.3 | 0.0460 | 0.00977 | 0.773 |
| | B = 0.061 | 11.7 | 0.1615 | 0.03429 | 0.709 |
| | (NaAc = 0.5) | 22.3 | 0.2330 | 0.04947 | 0.660 |
| | (NaCl = 0.25) | 42.0 | 0.3042 | 0.06459 | 0.614 |
| | | 51.3 | 0.3278 | 0.06960 | 0.610 |
| | | 60.0 | 0.3453 | 0.07331 | 0.608 |
| | | 72.0 | 0.3634 | 0.07716 | 0.600 |
| | | 96.5 | 0.3893 | 0.08263 | 0.584 |
| | | ... | 0.4710 | 0.10000 | ... |

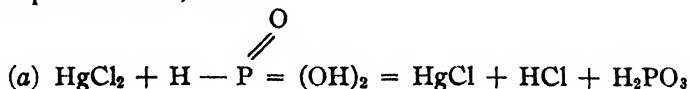
TABLE I (continued).

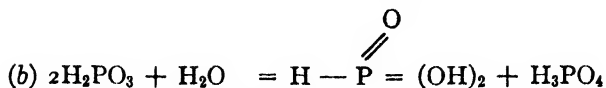
| Expt. No. | Initial concn. | <i>t</i> in hours. | HgCl in grams. | <i>x</i> in mols. | <i>K</i> . |
|-----------|-------------------------|--------------------|----------------|-------------------|------------|
| 5..... | A = 0.1 | 3.1 | 0.0386 | 0.00820 | 0.466 |
| | B = 0.061 | 12.4 | 0.1192 | 0.02531 | 0.445 |
| | (NaAc = 0.5) | 22.9 | 0.1800 | 0.03822 | 0.418 |
| | (NaCl = 0.5) | 42.5 | 0.2535 | 0.05382 | 0.408 |
| | | 63.8 | 0.2993 | 0.06355 | 0.389 |
| | | 74.3 | 0.3168 | 0.06726 | 0.385 |
| | | 86.4 | 0.3336 | 0.07083 | 0.380 |
| | | 99.0 | 0.3475 | 0.07378 | 0.376 |
| | | 119.4 | 0.3677 | 0.07807 | 0.376 |
| | | ... | 0.4710 | 0.10000 | ... |
| 6..... | A ₁ = 0.0985 | 12.5 | 0.0710 | 0.01507 | 0.229 |
| | B ₁ = 0.0610 | 22.6 | 0.1146 | 0.02433 | 0.229 |
| | (NaAc = 0.5) | 47.2 | 0.1894 | 0.04021 | 0.225 |
| | (NaCl = 1.0) | 69.3 | 0.2342 | 0.04977 | 0.219 |
| | | 108.6 | 0.2890 | 0.06136 | 0.215 |
| | | 143.0 | 0.3220 | 0.06837 | 0.215 |
| | | ... | 0.4638 | 0.09850 | ... |
| 7..... | A = 0.0985 | 28.0 | 0.0726 | 0.01541 | 0.106 |
| | B = 0.0610 | 53.3 | 0.1235 | 0.02622 | 0.107 |
| | (NaAc = 0.5) | 77.3 | 0.1600 | 0.03397 | 0.106 |
| | (NaCl = 2.0) | 102.4 | 0.1916 | 0.04068 | 0.105 |
| | | 146.0 | 0.2355 | 0.05000 | 0.105 |
| | | 197.4 | 0.2708 | 0.05749 | 0.103 |
| | | ... | 0.4638 | 0.09850 | ... |

Discussion of the Results.

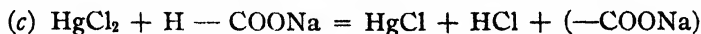
It is evident from Expts. 1, 2 and 7 that fairly concordant velocity constants may be obtained if the reaction proceeds under favorable conditions. It is also interesting to note that as the initial concentration of the sodium chloride is increased from 0.0 in Expt. 3 to twice normal in Expt. 7, the velocity coefficient gradually approaches constancy until in Expt. 6 the difference between the first and the last figures is only about 6%; also the total effect of the sodium chloride in the lowering of the magnitude of the velocity coefficient is seen to vary gradually from approximately 1.8 in Expt. 1 to 0.105 in Expt. 7. As far as the constants of Expts. 1, 2, 6 and 7 show, then, the reaction between mercuric chloride and sodium formate is evidently one of the second order, and it only remains to make the theory fit the figures.

The reaction between mercuric chloride and sodium formate may be represented in a similar manner to the one between mercuric chloride and phosphorous acid, thus:

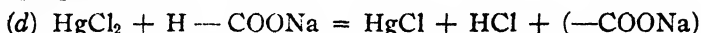




where reaction (b) is assumed to be practically instantaneous. Similarly:



In (a) we have a well-known compound formed, hypophosphoric acid, readily hydrated and incapable of reducing mercuric chloride except indirectly as indicated in (b). But no such compound as $-\text{COONa}$ is known. However, two such radicals in their nascent state might unite to form one molecule of sodium oxalate. But it is well known that sodium oxalate does not have the property of reducing mercuric chloride under ordinary conditions. Moreover, no trace of oxalates could be detected at any stage of the reaction. The most plausible assumption, then, is that the secondary reaction is similar to (b); that is, two radicals at the instant of liberation combine with one molecule of water to form one molecule of sodium formate and one of sodium hydrogen carbonate which is at once decomposed by the hydrochloric acid generated at the same time. The reactions, although occurring simultaneously, may be represented by the following equations:



Denoting the molal concentration of the mercuric chloride by A, that of the sodium formate by B, and by x the amount of the reacting substances decomposed, or the amount of mercurous chloride formed at time t , we have

$$\frac{dx}{dt} = K(A - X)(B - X + \frac{1}{2}X)^1$$

$$\frac{dx}{dt} = \frac{1}{2}K(A - X)(2B - X)$$

$$K = \frac{(2)(2.3)}{(2B - A)t} \log \frac{A(2B - X)}{2B(A - X)}$$

Summary and Conclusion.

1. It has been shown fairly conclusively, both experimentally and theoretically, that the reaction between mercuric chloride and sodium formate, like that between mercuric chloride and phosphorous acid, is one of the second order.

2. The retarding influence of the sodium chloride formed in the reaction is remarkable. Its effect, however, was reduced to a minimum by working, on the one hand, with dilute solutions of mercuric chloride, and, on the

¹ Since for every two molecules decomposed one molecule is regenerated, see also *Am. J. Sci.*, 35, 353-368 (1913).

other hand, by adding a large excess of sodium chloride initially to the reaction mixture, so that the amount of sodium chloride formed in the reaction was rendered negligible. Under these conditions concordant velocity constants were obtained as may be seen from Expts. 1, 2 and 7.

The experimental part of this work was begun at the Kent Chemical Laboratory of Yale University.

SEATTLE, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]
THE EFFECT UPON THEIR SOLUTION TENSIONS OF DISSOLVING THE ALKALI AND ALKALI EARTH METALS IN MERCURY, AND THE CONSTITUTION OF SUCH SOLUTIONS.

BY GEORGE MCPHAIL SMITH.

Received November 2, 1914.

In a discussion of the constitution of liquid amalgams, C. H. Desch¹ makes the following statements: "In simple eutectiferous series, in which the freezing-point curve shows no indication of the formation of compounds, we may safely accept the conclusion arrived at by the three methods described above (*i. e.*, the cryoscopic, vapor-pressure, and electromotive-force methods), that the dissolved metals are monatomic. *In series in which compounds occur, it remains as yet an open question whether the same condition prevails, or whether compounds containing a single atom of the dissolved metal in each molecule, are also present.*"² The only experimental method which gives any indication of a definite answer to this question is that of measuring the velocity of diffusion in liquid metals." He then proceeds to describe a portion of a paper by the writer³ in which this method is developed by the latter by means of M. von Wogau's⁴ experimental measurements of the rate of diffusion of various metals in mercury, and in which it is shown by this method that, in the case of the alkali and alkali earth amalgams, such compounds do actually exist in the mercurial solutions.⁵

In the above-mentioned paper,³ however, another experimental method is also developed, which, although it is at least capable of furnishing confirmatory evidence of the same thing, was in that paper apparently not explained sufficiently in detail. It is with the purpose of furnishing a clearer exposition of the latter method that the present paper is written.

¹ "Text-Books of Physical Chemistry," edited by Sir William Ramsay; "Metallography," by Cecil H. Desch, ed. 1910, p. 333f.

² The italics are the writer's.

³ G. Mc. P. Smith, *Z. anorg. Chem.*, 58, 381 (1908).

⁴ Max von Wogau, *Ann. Physik*, 23, 345 (1907).

⁵ The diffusion method as applied to the study of the constitution of metallic solutions has subsequently been placed upon a firm theoretical basis (cf. G. Mc. P. Smith, *THIS JOURNAL*, 36, 859 (1914)).

When a metal is immersed in a salt solution (in which, if present at all, its ions are limited in concentration), the solution tension of the metal tends to drive some of its ions into the solution, whereat the latter becomes positively charged, and the metal negatively charged. These charges give rise to a force component, which on the one hand tends to prevent the entrance of more positive ions into the solution, and on the other hand seeks to drive the positive ions in the solution back to the metal. One of two things must now take place. Either the solution tension of the metal is exactly compensated by the electrostatic charges, in which case there results an equilibrium; or, as a result of the magnitude of the solution tension, the electrostatic charge attains so high a value, that other positive ions which are contained in the solution are forced out of it and deposited on the metal.

In general, when a metal is immersed in a salt solution of another metal (which may or may not contain its own ions), the ions of the second metal will separate the more readily, the higher their own concentration, the greater the solution tension of the first metal, and the lower the ionic concentration of the first metal. If we designate the electromotive force necessary for the electrolytic separation of the first metal by ϵ , we have,

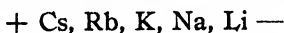
$$\epsilon = \frac{RT}{n} \ln \frac{P}{p},$$

(in which R is the gas constant, T the absolute temperature, P the electrolytic solution tension of the metal, p the osmotic pressure of its ions, and n the valency of its ions), and the separation of the second metal must take place as soon as the osmotic pressure of its ions and the electrostatic pull are able to overcome the electrolytic solution tension of the second metal, *i. e.*, the relation,

$$\epsilon_1 > \epsilon_2, \text{ or } \sqrt[n_1]{\frac{P_1}{p_1}} > \sqrt[n_2]{\frac{P_2}{p_2}},$$

must hold, in which the index 1 refers to the first metal, 2 to the second metal, and n_1 and n_2 are the valencies of the two metals.

The electromotive series of the univalent alkali metals reads:



Disregarding their action upon water, we should expect each metal in the series, beginning at the positive end, to be capable of displacing from aqueous salt solutions any metal which follows it in the series, and, under like conditions, this displacement should take place the more readily, the farther apart the two metals stand in the series. In other words, we should expect, under ordinary conditions, to have the relation

$$\frac{P_+}{p_+} > \frac{P_-}{p_-},$$

and the more electropositive metal should displace the more electro-negative one from its salt solutions.

Now, the relative magnitudes of the above two expressions, on which depends the direction of the displacement, can be affected in two ways, with the possibility of reversing them altogether. First, the values of p_+ and p_- can be changed at will, by regulating the ionic concentrations, and, second, the values of P_+ and P_- can be altered by substituting metallic solutions, or compounds, of the metals, in place of the metals themselves.

To take a concrete example, it appears very probable that finely divided sodium and potassium might be found capable of readily displacing one another from concentrated aqueous salt solutions, were it not for the action of the metals upon the aqueous solvent. On providing, however, for very much lower solution tensions of the metals—by the substitution of liquid amalgams for the free metals—their action upon the water is almost entirely prevented, and the reversible displacement of sodium and potassium from their aqueous salt solutions can be realized without difficulty.

In the experiments to be detailed in this paper, each amalgam of the respective pairs, Na and K, Na and Rb, and Na and Cs, in dilute equimolar mercurial solution, was allowed to act at 24° upon the corresponding one of three equivalent aqueous solutions, containing equimolar quantities of NaCl and KCl, of NaCl and RbCl, and of NaCl and CsCl, respectively; and, as will be seen from the data in Table I, equilibria were attained in all cases.¹

TABLE I.—EQUILIBRIUM DATA AT 24° .²

| No. | Amalgam. | Total normal concentration of salt solution. | Quantity of solution taken. Cc. | Quantity of amalgam taken. G. | Equiv. fractions of salts present in the solution. | | Atomic fract. of the alkali metals in the amalgam. | | Equilibrium constant $\frac{(\text{MeHg}_2)(\text{NaCl})}{(\text{NaHg}_2)(\text{MeCl})}$ | Mean value. |
|-----|-----------|--|---------------------------------|-------------------------------|--|---------|--|------------------------|--|-------------|
| | | | | | (NaCl). | (MeCl). | (MeHg ₂). | (N. Hg ₂). | | |
| 1a | 0.167% Na | 4.000 | 50.0 | 50 | 0.50 | 0.50 | 0.2290 | 0.7710 | 0.297 | 0.31 |
| 1b | 0.28% K | 4.000 | 50.0 | 50 | 0.50 | 0.50 | 0.2461 | 0.7539 | 0.326 | |
| 2a | 0.167% Na | 4.000 | 25.0 | 57 | 0.50 | 0.50 | 0.2635 | 0.7364 | 0.358 | 0.37 |
| 2b | 0.62% Rb | 4.000 | 25.0 | 50 | 0.50 | 0.50 | 0.2739 | 0.7260 | 0.377 | |
| 3a | 0.167% Na | 4.000 | 25.0 | 25 | 0.50 | 0.50 | 0.3244 | 0.6755 | 0.480 | 0.49 |
| 3b | 0.98% Cs | 4.000 | 25.0 | 25 | 0.50 | 0.50 | 0.3295 | 0.6705 | 0.491 | |

Now, at equilibrium, we have in the cases of these univalent metals the relationships, $P_{\text{Na}}/p_{\text{Na}} = P_{\text{Me}}/p_{\text{Me}}$; and, since $p_{\text{Na}} = p_{\text{Me}}$ in each

¹ Full details of these experiments have been published elsewhere by the writer (cf. *Z. anorg. Chem.*, **58**, 381 (1908); *Z. physik. Chem.*, **73**, 424 (1910)).

² The general formula MeHg_x is in this table used to represent either hydrargyride molecules (each containing only one atom of the amalgamated metal), or simply monatomic molecules of Me. In the latter case $x = 0$.

of the equimolal mixed-salt solutions employed in these experiments,¹ it follows that, in each amalgam at equilibrium, $P_{\text{Na}} = P_{\text{Me}}$. If, now, we are justified in the conclusion that, in dilute mercurial solution, the solution tension of a given alkali metal is roughly proportional to its concentration in the metallic solution,² then we are in a position to calculate the relative magnitudes of the solution tensions of these four metals in their dilute equimolal mercurial solutions. We have, at 24°, the relationships:³

$$P_{(\text{Cs})} = \frac{0.6730}{0.3270} P_{(\text{Na})}; \quad P_{(\text{Rb})} = \frac{0.7312}{0.2688} P_{(\text{Na})}; \quad P_{(\text{K})} = \frac{0.7625}{0.2375} P_{(\text{Na})};$$

$$\text{i. e., } P_{(\text{Na})} : P_{(\text{Cs})} : P_{(\text{Rb})} : P_{(\text{K})} = 1.00 : 2.06 : 2.72 : 3.21$$

It is thus seen that the solution-tension magnitudes of the free metals—which decrease in the order, Cs, Rb, K, Na—are, in the case of the first three metals, reversed upon dissolving the metals in an excess of mercury; they then decrease in the order K, Rb, Cs, Na. The same is true of the alkali earth metals: while the solution tensions of the free metals decrease in the order Ba, Sr, Ca, those of the metals in equimolal liquid mercurial solution decrease in the order Ca, Sr, Ba. It may be added that lithium, the least electropositive of the free alkali metals, becomes, in mercurial solution, the most electropositive of them all.⁴

Taken in connection with the contents of our introductory paragraph, these facts are regarded by the writer as furnishing very good evidence that dilute mercurial solutions of the alkali and alkali earth metals are solutions of mercury compounds of the respective metals. It has been shown by Ramsay,⁵ Heycock and Neville,⁶ G. Meyer,⁷ and others, that dilute mercurial solutions of metals are governed by the same laws with respect to the depression of the vapor pressure, the freezing point, etc., of the solvent, as are ordinary dilute solutions. Therefore, upon dissolving small, equimolal quantities of the alkali or alkali earth metals in equal, large quantities of mercury, if, as has often been assumed,⁸ they exist in solution in the form

¹ Cf. G. McP. Smith, *THIS JOURNAL*, 32, 502 (1910); 35, 39 (1913).

² Cf. G. Meyer, *Z. physik. Chem.*, 7, 447 (1891); T. W. Richards and R. N. Garrod-Thomas, *Ibid.*, 72, 165 (1910). It would, however, be more exact to consider the solution tension of the alkali metal as proportional to the concentration of MeHg_x in the dilute solution; but in the case of very dilute amalgams both considerations lead to results that are practically identical (cf. F. Haber, *Z. physik. Chem.*, 41, 399 (1902)).

³ The symbols $P_{(\text{Na})}$, etc., are used to indicate the relative solution-tension magnitudes of the metals in dilute equimolal mercurial solutions, such as those listed in the first column of Table I.

⁴ Concerning the behavior of the alkali earth metals and of lithium, Cf. G. McP. Smith, *Am. Chem. J.*, 37, 507 (1907); *Z. anorg. Chem.*, 58, 381 (1908).

⁵ *J. Chem. Soc.*, 55, 521 (1889).

⁶ *Ibid.*, 55, 666 (1889); 57, 376 (1890).

⁷ *Z. physik. Chem.*, 7, 447 (1891).

⁸ G. Meyer, *Ibid.*, 7, 447 (1891); M. von Wogau, *Ann. Physik*, 23, 345 (1907).

of free monatomic molecules, then we should expect their solution tensions to be indeed lowered, but in a more or less uniform manner; the relative magnitudes of their solution tensions should not be greatly altered. If, however, they enter into combination with mercury to form compounds containing only one atom of the amalgamated metal to the molecule, and if it is these compounds which are present in solution in the excess of mercury, then we should expect the solution tensions of the metals to be lowered to a very much greater degree, and *not* uniformly, but differently, depending upon the relative affinities of the metals for mercury.¹ The latter is what actually does happen; and, moreover, it would be difficult to explain the analogous behavior in this respect of the metals K, Rb, and Cs, on the one hand, and of Ca, Sr, and Ba, on the other—the members of two neighboring triads in the periodic system—on any other basis than that of the existence in mercurial solution of the corresponding members of the two triads in the form of analogously constituted compounds. Furthermore, it is well known that alkali metals are capable of entering into combination with mercury, even at ordinary temperatures, with the formation of crystalline compounds; and, *in the light of the mass law, it would indeed be a remarkable fact if such compounds were caused to undergo dissociation by the addition of a large excess of one of their constituent metals.*

In conclusion it may be added that the writer² has recently succeeded in showing, by means of the diffusion method already referred to, that, in mercurial solutions of these metals, the compounds present very probably correspond to the following formulas, in which, it will be noted, each compound contains but one atom of the amalgamated metal to the molecule: LiHg_3 , NaHg_5 , KHg_6 , RbHg_6 , CsHg_6 , CaHg_5 , SrHg_6 , and BaHg_6 .³

URBANA, ILL.

¹ The solution tensions of these metals in their amalgams are best explained as being due to the presence of their free monatomic molecules in the mercurial solutions; these metals are present in the mercury either wholly in the free state, or only partially so. In the latter event, we have the equilibrium: $\text{MeHg}_n \rightleftharpoons \text{Me} + n\text{Hg}$; and in dilute liquid amalgams mercury is present in such great excess, that $(\text{Me})/(\text{MeHg}_n) = \text{const.}$; that is, in the case of a given metal, C_{Me} , and therefore P_{Me} , is proportional to the total concentration of the metal in the dilute solution.

But, for the different metals in their dilute equimolar mercurial solutions, the different values of $(\text{Me})/(\text{MeHg}_n)$ depend upon the different degrees of dissociation of the compounds, MeHg_n , and these in turn depend upon the different affinities of the metals for mercury.

² THIS JOURNAL, 36, 859 (1914); *Z. anorg. Chem.*, 88, 161 (1914).

³ The crystals of the approximate composition KHg_{12} , etc., which have been mentioned in the literature (cf. e. g., Kerp and Böttger, *Z. anorg. Chem.*, 25, 1 (1900); Smith and Bennett, THIS JOURNAL, 32, 622 (1910)), are probably solid, or semi-solid solutions of the above compounds with mercury.

[CONTRIBUTION FROM THE WOLCOTT GIBBS LABORATORY OF HARVARD UNIVERSITY.]

A NEW THERMOCHEMICAL METHOD FOR SUBDIVIDING ACCURATELY A GIVEN INTERVAL ON THE THERMOMETER SCALE.

BY THEODORE W. RICHARDS AND THORBERGUR THORVALDSON.

Received November 16, 1914.

Heretofore the scientific world has relied primarily for its exact temperature scale upon the careful study of the expansion of hydrogen made at the Bureau des Poids et des Mesures. The reduction of this hydrogen scale to the true thermodynamic scale has been the subject of much interesting discussion.¹ But for several reasons, which need not be amplified here, the outcome is not wholly satisfactory, hence new methods of fixing the standard scale are earnestly desired. The linear temperature coefficient of the electrical conductivity of platinum is being strongly advocated by some as the standard, and seems at present to possess several advantages.² Nevertheless, this is no reason for withholding other suggestions; and, accordingly, the present paper describes an entirely new method of subdividing a small interval, which relies upon a thermochemical application of the first law of thermodynamics.

We were led to this method by inconsistencies amounting sometimes to over half of 1% in accurately conducted thermochemical experiments. These were numerous, involving heats of combustion, heats of dilution, heats of neutralization, and heats of solution of metals. The cause of the trouble might have been either (a) in experimental error, (b) in the thermodynamic reasoning involved, (c) in the measurement of the heat capacities or (d) in the measurement of the temperatures; but careful study led us to reject alternatives (a), (b) and (c). Accordingly, (d), only, remained; *i. e.*, the temperature scale must be in error. The irregularities were of such a character as to seem to show that the 18°-point on our standard thermometers (which had been calibrated with considerable care in Paris) was not exactly half-way thermodynamically between the 16° and the 20° point.

Therefore, it occurred to us that phenomena capable of showing such an inconsistency could be used, working backwards, to calibrate the thermometers; and, accordingly, a very simple reaction was chosen for this purpose. The problem was simply to conduct this reaction at various temperatures, in such a way that the final temperature of one trial should be the initial temperature of the next, thus covering the whole interval to be

¹ See for example, E. Buckingham, Bureau of Standards, Reprint No. 57 (Vol. 3, 1907). Burgess, *J. Chim. Phys.*, 11, 529 (1913).

² Jaeger and von Steinwehr, *Ann. der Phys.*, [4] 43, 1165 (1914) and others.

studied step by step in a way analogous to the Ostwald calibrator for a buret.

The heat of dilution of hydrochloric acid was chosen, on account of its ease of measurement, its easily regulated magnitude, and the comparatively simple nature of the heat-capacity problem involved. The acid was diluted calorimetrically in an apparatus described in detail in a previous paper;¹ the device was found to give very consistent and satisfactory results. By choice of varying initial concentrations of acid and of varying final concentrations, one can obtain at will a temperature-change anywhere from a few thousandths to several tenths of a degree—exactly such ranges as are likely to be required.

In the case to be described, acid of the precise concentration $\text{HCl} \cdot 20\text{H}_2\text{O}$ (9.18% or about 2.64 normal) was diluted with exactly 80 H_2O , causing it to become about 0.57 normal. This reaction gives enough heat to raise the total amount of liquid about 0.25° , a very convenient interval to use as a sort of thermodynamic yard-stick in subdividing the interval of 4° needed in thermochemical investigations.

Sixteen successive temperature increments during the dilution of successive portions of this sort, covering the whole scale between 16° and 20° , were as follows after correction for the heat of stirring (0.0005° per experiment): 0.2505° , 0.2520° , 0.2535° , 0.2535° , 0.2550° , 0.2550° , 0.2565° , 0.2575° , 0.2585° , 0.2575° , 0.2590° , 0.2585° , 0.2600° , 0.2595° , 0.2615° , 0.2605° . All these temperatures are given in terms of a standard scale, obtained after due correction from carefully standardized thermometers of excellent manufacture. It is evident that whereas at first the rise of temperature in the reaction seemed to have a temperature-coefficient of nearly 0.004° per degree, toward the end it seemed to possess no temperature-coefficient at all. This irregular performance suggests at once that something must be wrong with the thermometric scale; and the deviations are precisely in the same direction, and of the same order of magnitude as the earlier inconsistencies which led to this work.

If the heat capacity of the reacting substances remained unchanged during the dilution, the heat of dilution would remain constant, over the whole range, according to the well-known law of Kirchhoff.² In that case, the deviations of each of the numbers just given from their average would give at once the error of each number, and therefore the correction which should be applied to the thermometric readings over each short range. But with the particular reaction in question, this is not the case; the heat capacity of the system really diminishes appreciably during the reaction, and accordingly the heat of reaction increases appreciably

¹ Richards, Rowe and Burgess, *THIS JOURNAL*, **32**, 1179 (1910).

² See, for example, Richards, *THIS JOURNAL*, **25**, 209 (1903).

as the temperature rises. This increase is to be found by actually measuring the heat capacities of the factors and products—a measurement from which errors of the thermometer may be wholly eliminated by making the determination over the same range in each case. In this way it was determined that the heat capacity of $\text{HCl} \cdot 20\text{H}_2\text{O} + 80\text{H}_2\text{O}$ is 1778.5 and that of $\text{HCl} \cdot 100\text{H}_2\text{O}$ is 1772.3 (if the heat capacity of a gram of water is unity)—a loss of 6.2 calorie units of heat capacity during the reaction.¹ This signifies that the heat of dilution increases 0.00348° per degree, or 0.00087° for the quarter-degree interval between successive trials.² The value of the temperature-increment thus found for each stage of the dilution only holds exactly, however, in the ideal case in which (a) the apparatus, used for dilution has no heat capacity; (b), the change of heat capacity has no temperature-coefficient; and also when (c), the standard of reference of heat capacity (water), is likewise unchangeable over the total range concerned. The first and the last of these conditions obviously do not hold in the present case; but, fortunately, each is a matter susceptible of experimental solution. For: (a), the heat capacity of the apparatus, is easily calculated (in our experiments it was 1.643% of the total); (b), the change of heat capacity was found by actual measurement to be very nearly independent of temperatures between 16° and 20° ;³ again (c), the specific heat of the standard (water), has been determined by Barnes with great care by means of a platinum resistance thermometer (in a way practically independent of the hydrogen thermometer) to be 1.00105 at 16° if the value at 20° is taken as unity.⁴ This latter change is slight, amounting to only 0.000016° for each stage of the dilution—a relatively small proportion of the whole. In this case it almost exactly balances correction a. Correcting for these three minor influences, the theoretical increase in the temperature of each heat of dilution is found to be 0.00087° . If now we assume, as a preliminary step, that the first dilution should have given 0.25027° as its correct temperature rise, the successive theoretical heats of dilution will progress regularly as follows: 0.25027° , 0.2511° , 0.2624° , 0.2633° . The difference between each of

¹ These determinations were carefully made but they cannot be considered as more than preliminary ones; the details will be recorded in another place.

² Each rise of temperature due to heat of dilution was a trifle over the quarter of a degree, but they overlapped by a few thousandths of a degree, so that the 16 intervals really covered almost exactly 4° . The slight overlapping does not introduce any perceptible error.

³ If this is later found not to hold precisely, due correction can easily be applied.

⁴ N. B.—Although there may be some doubt about the *absolute* value of the specific heat of water, the *slope* of the curve at this point is probably quite near enough the true value for our present purpose. See Barnes, *Phil. Trans. (A)*, 199, 149 (1902).

⁵ This number was chosen by trial because it makes the correction at 20° the same as at 16° ; it assumes that this interval is indeed exactly 4.0000° .

these sixteen calculated values and the corresponding sixteen actual measurements mentioned on page 82, line 21, will give the error of the thermometer's reading over each of the short ranges, and the sum of all these partial errors down to any desired point will be the total errors to that point. In this way, the thermometric errors depicted in the following diagram were found in the special case chosen as an example, the values being plotted as ordinates, and the thermometer readings as abscissae.

Of course, since this is merely a relative matter, any one of the temperatures may be assumed as the standard of reference for these errors. As drawn, it was assumed that the correction at 17.14° was zero, in order to have about as many of the errors positive as negative; the reason of this choice will appear shortly. The shifting of the standard of reference shifts the whole curve bodily up or down, without affecting the algebraic

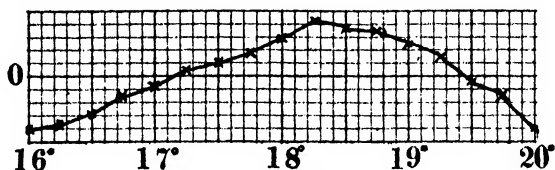


Fig. 1.—Errors of the thermometric scale in question. Scale readings are plotted as abscissas; errors (in thousandths of a degree) as ordinates.

differences of the corrections. For practical purposes it would be more convenient and less confusing to invert the curve (because a *plus* error means a *minus* correction) and to assume the lowest point of the resulting curve (18.25 in this case) as zero, so that all the corrections would be positive, and could be added directly to the thermometer reading.

A definite arbitrary change in the magnitude of the initial standard interval (in this case 0.25027) would change the general slant of the curve without altering its general character. Such a change alters the fundamental interval covering the whole range, and each part of this interval proportionately. The value 0.25027 was chosen because then the correction at 20° becomes the same as that at 16° , as already stated.

On the other hand, a change in the *increment* of the standard interval alters the character of the curve. This change is not arbitrary, but depends upon the measurements of the heat capacity, which must be executed with accuracy. It may be shown that the same actual degree of nicety is needed in this part of the work as in the work concerning the heat of

dilution, but lack of space forbids the detailed explanation. If the final curve is to have an accuracy in every part of 0.0005° , the change of heat capacity must be known to within about 0.25 calorie unit, which corresponds to an error of 0.001° over an experimental range of 4° , supposing that the calorimeter holds a liter of liquid.

It will be noted that this method does not attempt to fix the value of the standard interval with reference to the whole range $0-100^\circ$. The method gives only a means of *subdividing* any interval chosen as a standard (in this case the four degrees between 16° and 20°). To cover the whole range one would be required to carry out dilution experiments (or some other well-studied reaction) over the whole range. On the other hand, the method does provide a method for calibrating thermochemical thermometers, possessing just the degree of accuracy which is needed for thermochemical purposes.

The dilutions recorded in the special case above were verified by a similar series with a smaller rise of temperature (0.22), diluting $\text{HCl} \cdot 20\text{H}_2\text{O}$ to $\text{HCl} \cdot 121.5\text{H}_2\text{O}$. The curve in this series showed essentially the same features as the other, and need not be given in detail.

The shape of this curve given above is of more than passing interest, because it tells of corrections to be applied to the scale of a thermometer assumed to be trustworthy—the best that could be furnished a decade ago from a supposedly competent source. On the whole, it is seen to support the excellent work of the maker and of the standardizer; as recorded above, only one of the seventeen readings deviates more than 0.004° from its true value. But, nevertheless, the combined effect of these variations is a very serious matter, for the face-value of the interval between the true 16.000° and 18.000° is 2.007° , whereas between 18.000° and 20.000° is only 1.993° . In other words, there will be a discrepancy of 0.7% between the results obtained respectively over these two ranges: a very serious matter in accurate work. It was just such discrepancies which led to the undertaking of this new method; and it is pleasant to find that the new temperature scale removes many if not all of these discrepancies. But the chronicle of these details must be reserved for later communications. The question as to whether the errors are due merely to peculiarity in our standard thermometers, or are to be ascribed to the standard to which they in turn were referred, must be left to future research.

The results recorded above are only preliminary. The most difficult part of the performance (namely, the determination of the heat capacities of factors and products) can be determined once for all with great accuracy, and these figures can then be used by anyone, in any part of the world, for the computation of his results. The work required for the verification

of any thermometer will then consist simply in a series of dilutions (sixteen are obviously needed to cover 4° in 0.25° steps). This experimental work is very easily done, and with the adiabatic calorimeter is capable of great accuracy. Of course other reactions also, besides the heat of dilution of hydrochloric acid, could be used for this purpose, after they had been properly studied. Heat of neutralization of acids may be especially convenient. In case any interval appeared to be especially abnormal, it could be subdivided still further by a yet feebler reaction. We have already made further progress along these lines, and hope soon to publish a more complete account, which we hope may be really useful to chemists and physicists dealing with the difficult subject of exact thermometry.

We are greatly indebted to the Carnegie Institution of Washington, whose liberal grant alone made the work possible at this time.

Summary.

A new method for subdividing accurately any given interval on the thermometer scale is presented. This method depends upon the execution of a given simple reaction step by step over the range in question, somewhat analogously to the calibration of a buret with the Ostwald calibrator. Allowance must be made, of course, for the temperature-coefficient of the reaction, and other details dependent upon changing heat-capacity. The method is peculiarly suitable for the standardizing of short ranges, such as those used in thermochemistry.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE SEPARATION OF TUNGSTEN FROM MOLYBDENUM.¹

BY EDWARD ELLSWORTH MARBAKER.

Received October 8, 1914.

With the extensive introduction of tungsten and molybdenum into industrial chemistry in the form of the special steels and the filament of the incandescent electric lamp, the importance of these metals has been greatly increased from the standpoint of the analytical chemist.

It is a well-known fact that molybdenum always accompanies tungsten in its ores, and it shows a marked tendency to remain with the tungsten throughout the process of manufacture. This amount of molybdenum, although small, interferes to a great extent with the determination of the tungsten, and hence one of the important problems in modern analysis is to devise a separation of the two metals which will be easy to carry out and also be of the highest accuracy. Up to the present time there have

¹ From the author's Ph.D. thesis, 1914.

been suggested methods for the attainment of this end: Rose,¹ Pechard,² Smith and Reugenberg,³ Ibbotson and Brearley.⁴ In 1911, Mdivani⁵ announced a new method for the determination of tungsten which was based on the observation of Anthon,⁶ that when a tungstate solution is treated with a solution of stannous chloride, a yellow precipitate of normal tin tungstate, SnWO_4 , is formed, which is changed to the blue oxide of tungsten, W_2O_5 , on the addition of concentrated hydrochloric acid. Mdivani added to the tungstate solution, a solution of stannous chloride in concentrated hydrochloric acid and then boiled for a few minutes. The blue oxide was precipitated and, after settling, was filtered off, washed with hot water, dried, ignited to tungsten trioxide and weighed as such.

1. An Effort to Reproduce the Results of Mdivani.

Mdivani made up a solution for analysis by dissolving 2 g. of pure tungsten trioxide in strong ammonia and diluting to one liter. He treated 50 cc. of this solution, which contained 0.1 g. of WO_3 , with 20 cc. of a solution containing 50 g. of crystallized stannous chloride in 200 cc. concentrated hydrochloric acid. The blue precipitate which was thrown down was boiled up for a few minutes and then allowed to settle, after which it was washed by decantation with hot distilled water and finally ignited and weighed as tungsten trioxide.

A weighed sample of pure tungstic acid, which had been prepared for the purpose of making ductile tungsten lamp filament; was treated with strong ammonia. The attack was not complete, showing that the purity of the substance was doubtful; but the solution was filtered and made up to one liter. Samples of this solution were analyzed by evaporating to dryness three times with hydrochloric acid and nitric acid, baking at about 120° for fifteen minutes after each evaporation, then washing on to a filter with a hot ammonium nitrate solution, finally igniting and weighing. Fifty cc. of the solution were thus found to contain 0.1422 g. WO_3 . This value was obtained as the average of ten closely agreeing determinations.

A solution of stannous chloride was made according to the directions of Mdivani. Twenty cc. of the tin solution were added to 50 cc. of the ammonium tungstate solution, and the resulting blue precipitate was boiled for a few minutes and washed according to the directions of Mdivani. The pure water recommended for washing was found to be inadequate because it caused the formation of basic tin salts which could not be

¹ Rose, Treadwell-Hall, *Analytical Chemistry*, II, 3d ed., 1911, p. 296.

² Pechard, *Ibid.*, 295; *Compt. rend.*, 114, 173 (1892).

³ Smith and Reugenberg, *THIS JOURNAL*, 22, 772 (1900); Treadwell-Hall, 293.

⁴ Ibbotson and Brearley, *Chem. News*, 81, 13 (1900).

⁵ Mdivani, *Bull. Soc. Chem.*, [4] 9, 122 (1911).

⁶ Anthon, Dammer, *Handbuch*, 3, 659 (1893); *J. prakt. Chem.*, 9, 341 (1836).

washed out and hence gave rise to high results. This was easily remedied by washing the precipitates with a solution of hydrochloric acid made by adding 50 cc. of strong acid to a liter of boiling distilled water. The washed precipitates were thus entirely free from tin.

Four determinations resulted as follows:

WO₃ present, 0.1422 g.; WO₃ found, 0.1392, 0.1386, 0.1390 and 0.1387 g.

To determine the cause of these low results, the filtrate from one of the determinations, which was perfectly clear and colorless, was evaporated to dryness. Blue oxide of tungsten separated. This showed that either the precipitation had not been complete or that the acid of the wash water had caused some of the oxide to pass into solution. Subsequent results indicated that the latter was not the case. The small amount of blue oxide was transferred to a filter and washed with the dilute acid until the filtrate gave no test for tin on the addition of ammonia. The filter and its contents were then ignited, but instead of obtaining a small amount of yellow tungsten trioxide, there was present a mixture of the yellow oxide and a white substance which proved to be tin oxide. This would indicate that a combination had taken place between the tin and the tungsten, because all of the tin had been washed out of the precipitate so far as the tests on the filtrate showed. In order to eliminate the small amount of tin, the residue was carefully treated with ammonium chloride, as recommended by Rammelsberg,¹ which causes the tin to volatilize as stannic chloride, leaving the tungstic acid behind. The weight of this residue added to that of the main portion of the oxide brought the result into agreement with the theoretical.

2. The Action of Mdivani's Reagent on a Mixture of Ammonium Tungstate and Ammonium Molybdate.

When stannous chloride was added to a solution of ammonium molybdate a brown precipitate appeared. This rapidly dissolved in the excess of the reagent, the solution assuming a characteristic orange color, due to the reduction of the MoO₃ to Mo₂O₃. This is very different from the reaction which takes place in the tungstate solution, hence it seemed possible to effect a separation.

A solution of molybdenum trioxide in ammonia was made up and analyzed by the method of Chatard.² Ten cc. of the solution were found to contain 0.1164 g. MoO₃.

A solution containing 0.1164 g. MoO₃ and 0.1422 g. WO₃ was treated with 20 cc. of the tin solution and the resulting precipitate of W₂O₆ handled as outlined before. It was washed with the acid wash water until the washings gave no test for tin. The filter and its contents were ignited and weighed. A fairly close value for the tungsten was obtained.

¹ Rammelsberg, *Chem. News*, 9, 25 (1864).

² Chatard, *Ibid.*, 24, 475 (1871).

It was assumed at this point that the precipitate of tungstic acid contained no molybdenum, but a careful test was made to determine whether the filtrate containing the molybdenum contained any tungsten. This test was carried out as follows: An excess of metallic zinc was added to the solution and the tin was precipitated as metal. The solution changed color from orange to green. It was decanted from the tin, which was present in the form of a porous cake, and the tin washed several times with hot water. The clear green liquid was then evaporated on the hot plate, during which process the color changed to brown again. When the bulk of the solution had been decreased to about 150 cc. a few drops of nitric acid were added. It rapidly became colorless, showing that the molybdenum had been oxidized to the form of molybdate. Ammonia was then added in great excess. The precipitate of zinc hydroxide which first appeared dissolved in excess, leaving a small precipitate of iron and tin hydroxides. This was filtered out and reprecipitated. The filtrate was added to the main solution and the whole treated with acid to the point of neutrality. A small amount (3-5 cc.) of acetic acid was then added, followed by an excess of lead acetate. A precipitate of lead molybdate was formed which after settling, was filtered, washed with dilute acetic acid, ignited and weighed. This weight proved to be lower than the theoretical but the loss could not be accounted for, although the precipitate of tin metal, the iron and tin precipitate, and the filtrate from the lead molybdate were all tested with zinc and sulfocyanide, but no evidence of molybdenum was observed.

The ignited residue of lead molybdate was then tested with hydrochloric acid, according to the method of separation suggested by Ibbotson and Brearley.¹ The solution of the residue was complete, but on dilution no tungstic acid separated out, thus showing that the molybdenum was not contaminated with any tungsten and that, so far as the tungsten was concerned, the separation was complete.

It was found in other determinations, carried out in the same way, that the weight of the tungstic oxide was high, although all the tin had been removed by careful washing. The high results must then have been due to a small amount of molybdenum left in the tungsten. The precipitate of W_2O_6 was dissolved in ammonia containing a little hydrogen peroxide and reprecipitated with a second portion of the tin solution. The precipitation at this point was never complete, because the filtrate had a blue color. This was evaporated to dryness, the W_2O_6 washed out and ignited with ammonium chloride and finally weighed. This weight was added to that of the main precipitate and the sum of the two gave a somewhat low result, due probably to unavoidable losses in the process of analysis.

¹ Ibbotson and Brearley, *Chem. News*, 81, 13 (1900).

A series of results follows:

| Gram WO_3 present. | Gram WO_3 found. | Gram WO_3 present. | | Gram WO_3 found. |
|--------------------------------|------------------------------|--------------------------------|----------------|------------------------------|
| 0.1422 | 0.1426 | 0.1422 | Reprecipitated | 0.1412 |
| 0.1422 | 0.1414 | 0.1422 | | 0.1405 |
| 0.1422 | 0.1429 | 0.1422 | | 0.1414 |
| 0.1422 | 0.1434 | 0.1422 | | 0.1434 |
| 0.1422 | 0.1432 | 0.1422 | | 0.1428 |
| 0.1422 | Reprecipitated 0.1404 | 0.1422 | | 0.1415 |

Average, 0.1422

These results indicate a possible separation of tungsten from molybdenum, although they are not particularly concordant. The molybdenum was not determined, because at the moment there was no method available for the separation of the molybdenum from extremely large amounts of tin.

3. The Action of Mdivani's Reagent on a Mixture of Sodium Tungstate and Sodium Molybdate.

Mdivani states in his paper that the quantitative precipitation of tungsten may be carried out as well in solutions of sodium and potassium tungstate and molybdate as in solutions of the ammonium salts.

The solution of sodium tungstate used was made from a portion of the salt which had been prepared by fusing together the theoretical amounts of pure WO_3 and Na_2CO_3 and crystallizing the product. The solution contained 0.1489 g. WO_3 in each 10 cc. The solution of sodium molybdate was made by dissolving a sample of a salt, which had been made by Schuchardt, and afterwards recrystallized several times. This solution contained 0.1200 g. MoO_3 in each 10 cc.

A sample of the tungstate solution was measured out and treated with the usual amount of Mdivani's reagent. The blue precipitate appeared and was filtered off. The filtrate was colored blue, showing that the precipitation had not been complete. Several attempts were made to improve this precipitation by adding more reagent than usual and also by the addition of ammonium chloride, but without any favorable results.

A solution containing both tungstate and molybdate was then treated in the usual manner with the tin solution in order to determine the effect of the presence of sodium molybdate. The blue precipitate of W_2O_5 came down well and was weighed after filtering and washing. The filtrate in this case was orange colored, on account of the molybdenum present. A series of ten determinations was made and the results were so concordant and near the theoretical that it shows conclusively that for the amounts of tungstate and molybdate present a separation of tungsten and molybdenum can be effected by means of an acid stannous chloride solution. The results follow:

| Gram MoO ₃ present. | Gram WO ₃ present. | Gram WO ₃ found. |
|--------------------------------|-------------------------------|-----------------------------|
| 0.1200 | 0.1489 | 0.1492 |
| 0.1200 | 0.1489 | 0.1489 |
| 0.1200 | 0.1489 | 0.1490 |
| 0.1200 | 0.1489 | 0.1486 |
| 0.1200 | 0.1489 | 0.1486 |
| 0.1200 | 0.1489 | 0.1489 |
| 0.1200 | 0.1489 | 0.1492 |
| 0.1200 | 0.1489 | 0.1486 |
| 0.1200 | 0.1489 | 0.1489 |
| 0.1200 | 0.1489 | 0.1489 |

As in the case of the separation of tungsten and molybdenum using the ammonium salts, the molybdenum was not determined.

The tungsten trioxide obtained in the foregoing analyses was tested for molybdenum by the method of Debray¹ by passing over it dry hydrogen chloride at a temperature of 200°. A slight sublimate of the compound MoO₃.2HCl was formed, proving that a little molybdenum was present. On subsequent analysis by the method of Chatard it was found that the molybdenum contained in the tungsten trioxide from six determinations amounted to less than one milligram of MoO₃.

The fact that the separation takes place so easily is so at variance with the usual experience of analysts of tungsten compounds that it seemed very remarkable that the molybdate actually aids the precipitation of the tungsten, as it will be remembered that the precipitation of W₂O₆ from the tungstate alone is never complete. This was so peculiar that the effect of other salts on the precipitation was tried. The results of these tests were as follows:

| Salt present. | Gram WO ₃ present | Gram WO ₃ found. |
|---|------------------------------|-----------------------------|
| 0.1 g. K ₂ SO ₄ | 0.1489 | 0.1481 |
| 0.1 g. K ₂ SO ₄ | 0.1489 | 0.1488 |
| K ₂ CrO ₄ | 0.1415 | 0.1414 |
| 0.2 g. NaCl..... | 0.1489 | 0.1487 |
| 0.2 g. NaCl..... | 0.1489 | 0.1494 |

The filtrate from the tungsten in all of the foregoing determinations, except that containing chromium, was perfectly colorless. These results show that an accurate estimation of the tungsten in sodium tungstate can be made by the addition of any of the salts mentioned in the table.

In order to determine the availability of the method various amounts of sodium tungstate and sodium molybdate were taken. The results appear in the following table:

| Gram MoO ₃ present. | Gram WO ₃ present. | Gram WO ₃ found. |
|--------------------------------|-------------------------------|-----------------------------|
| 0.1200 | 0.0089 | 0.0089 |
| 0.1200 | 0.0149 | 0.0151 |
| 0.1200 | 0.0596 | 0.0592 |
| 0.1200 | 0.0900 | 0.0900 |

¹ Debray, *Compt. rend.*, 46, 1101 (1858).

| Gram MoO ₃ present. | Gram WO ₃ present. | Gram WO ₃ found. |
|--------------------------------|-------------------------------|-----------------------------|
| 0.1200 | 0.1200 | 0.1200 |
| 0.1200 | 0.1788 | 0.1786 |
| 0.1200 | 0.2100 | 0.2101 |
| 0.1200 | 0.2400 | 0.2397 |
| 0.1200 | 0.2700 | 0.2700 |
| 0.1200 | 0.3000 | 0.2998 |
| 0.0121 | 0.1500 | 0.1496 |
| 0.0241 | 0.1500 | 0.1497 |
| 0.0482 | 0.1500 | 0.1500 |
| 0.0724 | 0.1500 | 0.1504 |
| 0.0965 | 0.1500 | 0.1499 |

4. The Determination of the Molybdenum in the Filtrate from the Blue Oxide.

The filtrate from the tungsten contains all the molybdenum and a large amount of tin in the form of stannous and stannic chlorides. The tin was removed from the solution by means of metallic zinc, the filtrate was evaporated down to a small bulk, oxidized with nitric acid and treated with an excess of ammonia. The zinc hydroxide which was thrown down dissolved in excess. The molybdenum was then precipitated by lead acetate after the solution had been almost neutralized with HCl and finally treated with a small excess of acetic acid. The precipitate of lead molybdate was allowed to settle, filtered, washed with hot dilute acetic acid, and finally weighed. In every case the result was low.

Since the foregoing procedure failed to solve the problem of determining the molybdenum, a careful review of the literature was taken up in the hope that a method for determining molybdenum in a hydrochloric acid solution had been devised. Nothing of this nature was found in connection with any gravimetric method, but the discussion of the volumetric methods seemed to offer a means of solving the problem.

Randall¹ has shown that when a molybdate solution is passed through a Jones reductor and the reduced solution is caught in a ferric ammonium sulfate solution, decolorized by phosphoric acid, that the ferric iron oxidizes the molybdenum, and the ferrous iron thus formed may be titrated with standard potassium permanganate. This investigator proved that the molybdenum is completely reduced to the form of Mo₂O₃. Accordingly, a determination was carried out as follows: A portion of the sodium molybdate solution was measured out and treated with about 20 cc. of Mdivani's reagent. This gave rise to an orange colored solution, to which were added about 5 g. of pure 20-mesh zinc. The tin was deposited on the zinc as metal, and the green supernatant liquid was poured off, the tin washed with hot water, and then the solution and washings were heated to about 60°.

The reductor flask was charged with 20 cc. of the ferric alum solution

¹ Randall, *Am. J. Sci.*, [4] 24, 313 (1907).

and 20 cc. of the "titrating solution."¹ Fifty cc. of dilute hydrochloric acid (2.5% by vol. of the concentrated acid heated to 60°) were passed through the reductor, followed by the solution containing the molybdenum, and then 150 cc. of the warm acid and finally 150 cc. of hot distilled water.

The flask was removed from the reductor and the titration was carried out in the usual way with the permanganate² solution. The molybdenum solution before entering the reductor is green, while in the reductor the reduction is completed, although there is no noticeable change in color. When the green solution enters the ferric solution the color changes to red. This red solution is titrated with permanganate, but the red color offers no obstacle because, as the permanganate is added, this color disappears, and toward the end of the titration the color of the solution is a faint bluish green in which the end point is very easily seen. The end point has to be taken very quickly, as it is not at all permanent. However, the titration is one which is very easily carried out.

A number of such determinations were made with the following results:

| Gram MoO ₃ present. | Gram MoO ₃ found. | Gram MoO ₃ present. | Gram MoO ₃ found. |
|-----------------------------------|---------------------------------|-----------------------------------|---------------------------------|
| 0.1500 | 0.1505 | 0.1350 | 0.1354 |
| 0.1500 | 0.1505 | 0.1635 | 0.1632 |
| 0.1470 | 0.1476 | 0.1200 | 0.1198 |
| 0.1500 | 0.1498 | 0.1050 | 0.1051 |
| 0.1500 | 0.1498 | 0.1800 | 0.1801 |

They show that the separation of tin from molybdenum by means of metallic zinc is quantitative and that the method may be used to determine the molybdenum in the filtrate from the tungsten in the method of separation under consideration.

5. The Separation of Tungsten from Molybdenum.

The two processes outlined in the third and fourth sections of this paper were combined, and both constituents of the mixture of sodium tungstate and molybdate were determined.

The separation worked very well with quantities up to and including 0.3000 g. of each constituent. More than this amount gave rise to high results unless an inordinate amount of time was consumed in washing out the molybdenum from the tungsten. The high results can be more quickly corrected by treating the ignited residue of WO₃ with as many cc. of concentrated hydrochloric acid as there are centigrams of the residue and boiling for a few minutes. Then this may be diluted with three times its volume of hot water and allowed to settle. This process removes the contaminating molybdenum and leaves the tungsten pure. The filtrate containing the small amount of molybdenum is of course

¹ This consisted of 90 g. manganous sulfate, 650 cc. distilled water, 175 cc. syrupy phosphoric acid and 175 cc. concentrated sulfuric acid.

² Standardized against ferrous ammonium sulfate and also oxalic acid.

added to the main molybdenum solution. There seem to be no limits to the applicability of the molybdenum titration. When large amounts of molybdenum were present it was found advisable to make up to 250 cc. and work with portions of 50 cc. each. The latter method proved to be a great factor in reducing the time of the determination.

When moderate samples are used the whole process, involving the determination of both the constituents, can be carried out in about three hours. The greater part of this time is consumed in washing the tungsten precipitate and in evaporating the filtrate containing the molybdenum to a bulk which may be easily handled.

The results of ten complete separations follow:

| Gram WO_3 present. | Gram MoO_3 present. | Gram WO_3 found. | Gram MoO_3 found. |
|-------------------------|--------------------------|-----------------------|------------------------|
| 0.1005 | 0.1005 | 0.1001 | 0.1010 |
| 0.1500 | 0.1500 | 0.1496 | 0.1498 |
| 0.2000 | 0.2000 | 0.2004 | 0.1995 |
| 0.2520 | 0.2505 | 0.2526 | 0.2499 |
| 0.3015 | 0.3000 | 0.3016 | 0.2997 |
| 0.3500 | 0.3500 | 0.3508 | 0.3502 |
| 0.4005 | 0.4005 | 0.4008 | 0.3995 |
| 0.4500 | 0.4500 | 0.4508 | 0.4495 |
| 0.4995 | 0.4995 | 0.4999 | 0.4994 |
| 0.3000 | 0.3000 | 0.3000 | 0.2996 |

Summary.

Tungsten and molybdenum, in the form of their sodium salts, may be quickly and easily separated, the course of analysis being as follows:

To a boiling solution containing the tungstate and molybdate of sodium in appropriate amounts add the tin solution (50 g. $SnCl_2 \cdot 2H_2O$ dissolved in 200 cc. concentrated HCl) in the proportion of 20 cc. for each 0.15 g. WO_3 present. This amount of the reagent should be carefully regulated, because less will not effect a complete separation, and more will be correspondingly harder to handle in the determination of the molybdenum. The dilution of the solution for analysis should be kept between 60 cc. and 300 cc., depending on the amount of tungsten present. After boiling a few minutes allow the blue precipitate of W_2O_5 to settle and then pour the orange supernatant liquid through a filter. Wash the precipitate thoroughly by decantation with hot 5% hydrochloric acid until the washings give no test for molybdenum by the zinc and thiocyanate method. Bring the precipitate on the filter and allow to drain. If the amount of precipitate is small the filter may be ignited wet, but if the amount be large it is better to heat it until the greater part of the water has been driven off. Place the filter in a porcelain crucible and ignite gently to WO_3 . Cool in a desiccator and weigh.

The filtrate and wash water are united and the whole evaporated to a small bulk. If the amount of tungsten and molybdenum taken has been

large, cool and dilute to 250 cc. and use aliquot portions of 50 cc. To this solution add from 5-10 g. of 20 mesh zinc. The tin will come out as metal. Pour off the green solutions when the precipitation of the tin is complete (this takes about ten minutes), and wash the cake of tin several times with hot water. Unite the filtrate and wash water and heat to 60°. Pass through the reductor in the order named, 50 cc. dilute HCl,¹ the solution containing the molybdenum, 150 cc. 2.5% (vol. conc. HCl), and finally 150 cc. hot distilled water. These pass into the flask of the reductor, which has been previously charged with 20 cc. 10% ferric ammonium sulfate and 20 cc. of the "titrating solution." This solution is next titrated with approximately 0.1 N potassium permanganate and the amount required calculated to MoO₃.

If it is desired to determine the amount of tungsten in a sodium tungstate solution, add to that solution a quantity of sodium chloride solution, and proceed as when molybdenum is present.

A fairly accurate separation of tungsten and molybdenum may be effected when they are present as ammonium salts, but the method is not to be highly recommended.

UNIVERSITY OF PENNSYLVANIA,
PHILADELPHIA, PA.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD COLLEGE.]

THE MOLECULAR WEIGHT OF SODIUM CARBONATE AND THE ATOMIC WEIGHT OF CARBON REFERRED TO SILVER AND BROMINE.

By THEODORE W. RICHARDS AND CHARLES R. HOOVER.

Received November 19, 1914.

Investigations concerning radioactivity have increased rather than diminished the interest in atomic weights. The possibility indicated by recent research that variations in these figures may exist in radioactive elements² stimulates further research in all directions concerning these quantities; for such variations cannot be due to chance, but must have fundamental cause. To be sure, no valid evidence of variation in any value except that for lead has as yet been found; but whether or not the atomic weights vary in a few cases, they still probably remain the most fundamental figures which come within our scientific ken. Therefore, no amount of trouble is too great to secure complete and satisfactory knowledge of them.

¹ Containing 2.5% by volume of the strong acid.

² Richards and Lambert, *THIS JOURNAL*, 36, 1329 (1914); also *Z. anorg. Chem.*, 88, 429 (1914), and *Science* (June 5, 1914), p. 831. This conclusion has been supported also by Soddy (*Proc. Chem. Soc.*, 30, 134 (1914)), by Maurice Curie (*Compt. rend.*, 158, 1676 (1914)), and by Hönigschmid and Mille. S. Horovitz (*Ibid.*, p. 1786); also *Z. Electrochem.*, 20, 319 (1914).

It is well recognized by everyone conversant with this matter that as many different methods as possible for determining each atomic weight should be employed. F. W. Clarke has often emphasized this point. The difficulty in carrying out this recommendation is that so few substances lend themselves to accurate analysis. Crystalline precipitates always carry down some of the mother liquor from which they were prepared, and hence many usual analytical methods are not permissible, when great accuracy is required. For this reason, and so as to get consistent and comparable results with different metals, the analysis of the chlorides and bromides has been one of the chief methods employed at Harvard—because the spongy nature of the silver halides makes it possible to wash them with unusual thoroughness. But some means of verifying these results by comparison with an entirely different standard would be highly welcome. For this purpose a new process, involving cross-reference, has recently been carried out in the Wolcott Gibbs Memorial Laboratory; and the present paper describes this new method of attack.

The plan was simply this: the purest sodium carbonate was to be weighed with scrupulous care, dissolved in water, and exactly neutralized with hydrobromic acid. The amount of silver necessary to precipitate this hydrobromic acid was then to be determined by the usual process. In this way the chemical equivalence between the weights of sodium carbonate and silver could be simply determined, and the silver halide standard referred directly to an entirely new substance, namely, sodium carbonate. The accuracy of the process turned, of course, upon obvious criteria: first, the purity of the sodium carbonate and hydrobromic acid; secondly, the complete and exact neutralization without loss of material; and thirdly, the purity of the silver. The sodium carbonate, silver and silver bromide alone were weighed; but the hydrobromic acid obviously had to be prepared in a state free from every trace of other acids as well as from bases. As will be seen, the outcome was very satisfactory.

Preparation of Materials.

In an investigation of this kind the details of experimentation are of the utmost importance, therefore the necessary minutiae are given below.

Three different specimens of sodium carbonate were prepared: the first simply by many recrystallizations from water in platinum vessels; the second from recrystallized hydroxide made by the reaction of sodium bromide on silver oxide; and the third from sodium amalgam electrolytically produced from hydroxide resulting from the reaction of barium hydroxide on sodium sulfate. In making the first sample 3 kg. of "C. P." sodium carbonate were dissolved in pure water, filtered while cold through hardened filter paper, and at first recrystallized four times from pure water in porcelain dishes with centrifugal washing and draining.

The solution of the crystals was again filtered, as before, through washed filter paper, and recrystallized five times in platinum vessels, again with centrifugal draining and washing. The solution of this ninth crop of crystals was finally filtered through the platinum mat of a carefully prepared Gooch-Munroe crucible, and recrystallized, making ten crystallizations in all. The last crop of crystals, contained in a platinum dish, was dehydrated in a vacuum desiccator over fused sodium hydroxide, and was called Sample A.

As briefly suggested above, the second sample B was prepared in a very different way. Sodium hydroxide (previously twice recrystallized) was added in excess to twice recrystallized silver nitrate. The washed precipitate of oxide was treated with a solution of sodium bromide which had been five times recrystallized as hydrate. The resulting sodium hydroxide solution was then once recrystallized from concentrated solution by strong cooling, and was transformed into sodium carbonate by passing pure carbon dioxide into the solution through an inverted platinum funnel. The solution was filtered through a platinum mat, and the salt was thrice crystallized. All these operations were carried out in platinum, except the crystallization of sodium hydroxide, which was carried out in silver.

For the sake of especial care, the preparation of the third sample, C, involved yet different processes. Sodium sulfate was added in slight excess to barium hydroxide, each having been previously four times recrystallized. The solution was decanted from the precipitate through a platinum filter and the resulting sodium hydroxide crystallized by cooling. A solution of this sodium hydroxide was electrolyzed in an amalgamated iron dish. The solid amalgam, after thorough washing, was partly decomposed by water, and the solution was evaporated to crystallization. The pure caustic alkali was transformed into carbonate as in the case of Sample 2, and the salt thus obtained was thrice recrystallized. All operations, except the electrolysis in the iron dish, were carried out in platinum or silver.

The hydrobromic acid was prepared from an especially pure sample of potassium bromate, which we owed to the kindness of Edward Mallinckrodt, Jr., of St. Louis. Three kilograms of this material (which showed only a trace of chlorine and no iodine) were three times recrystallized in porcelain; even the first crystals gave no test for chloride. Portions of the very pure product were decomposed to bromide by heating in platinum, and the bromide was fused. Proper quantities of bromate, bromide and very pure redistilled diluted sulfuric acid were gently heated in a glass-stoppered distilling flask. The pure bromine which distilled off was twice redistilled from the similar potassium bromide, and passed with hydrogen over hot platinized asbestos. The hydrobromic acid thus

formed was dissolved in pure water, concentrated, and three times redistilled through a quartz condenser.

Three samples of silver were used. The first was made from pure silver nitrate by a well tested method.¹ The salt, five times recrystallized, was reduced with ammonium formate prepared from redistilled ammonia and formic acid. The metal was thoroughly washed, dried and fused in hydrogen on a boat of pure lime made from six times recrystallized calcium nitrate. The buttons were then etched with nitric acid, washed with ammonia and much water, and dried at 400° in a vacuum.

The second sample was prepared with twice as much care, but appeared to be no purer. Silver nitrate, ten times recrystallized, was reduced in a silver dish with ammonium formate made by passing ammonia from redistilled ammonium hydroxide contained in a platinum retort into formic acid, twice redistilled in quartz, contained in a gold flask. The silver powder was washed many times with purest water, then fused and dried as in Sample 1.

A third sample of silver, prepared by Dr. H. H. Willard in our research on lithium perchlorate, was used in analyses Nos. 4 and 5.²

The quantitative identity of these three samples is evidence that all were as pure as possible.

In a research of this kind, involving exact neutralization, especial pains must be taken, not only with the solid substances concerned, but also especially with the water and gases which are employed. Water was thrice distilled, alkaline permanganate and a few drops of sulfuric acid being used in successive distillations, as usual. A thoroughly washed condenser of block tin was employed. Especial care was taken to exclude the products of combustion of the burners from the product. For much of the work, where carbon dioxide must be rigorously excluded, the water from the final distillation was condensed in such a way that it was collected cold in a stream of air wholly freed from carbon dioxide. The air used for this purpose, and in other cases where carbon dioxide must be excluded, was drawn direct from the vent supplying the filtered air to the laboratory before its entry into the room, and was washed and driven by a water blast through a long tube of copper oxide and through Emmerling towers containing, in succession, solution of copper sulfate, potassium permanganate dissolved in dilute very pure phosphoric acid, pure permanganate made alkaline by potassium hydroxide which had been fused to drive out volatile substance, and concentrated potassium hydroxide; then over solid, fused potassium hydroxide, and, finally, where it was

¹ Richards and Wells, Carnegie Inst. of Washington, Publication No. 28, 19 (1905); *THIS JOURNAL*, 27, 475 (1905); *Z. anorg. Chem.*, 46, 74 (1905).

² Richards and Willard, Carnegie Inst. of Washington, Publication No. 125, 16 (1910), Sample A.

necessary to have especial purity and absence of moisture, over fused potassium hydroxide and resublimed phosphorus pentoxide, and over hot copper oxide, being filtered at last through a porous cup to retain dust particles.¹ The apparatus was, of course, constructed entirely of glass with fused or ground joints.

Carbon dioxide was generated in an Ostwald apparatus by the action of diluted, redistilled hydrochloric acid on selected pieces of pure marble. The gas was first passed through three towers containing sodium bicarbonate solution, and afterwards through three towers of boiled, concentrated sulfuric acid to which a trace of potassium dichromate had been added, and, finally, through a long U-tube of resublimed phosphorus pentoxide.

In one preliminary experiment nitrogen was used. This was prepared by the Wanklyn method of passing ammonia and air over heated copper. The apparatus for this purpose was kindly loaned us by Professor Baxter and Dr. C. J. Moore. Glass stopcocks were lubricated with a very small amount of a mixture of viscous paraffines containing a little pure melted rubber, as suggested by Ramsay. They were so arranged that either pure air or carbon dioxide could be passed, separately or mixed, through the familiar Harvard bottling apparatus;² and also when needed through vessels in which the solution of the sodium carbonate and the evaporation of the bromide were carried out.

Preparation of Sodium Carbonate for Analysis.

The almost anhydrous carbonate, after long drying in a desiccator over fused caustic alkali, was placed in a weighed platinum boat, covered with a piece of platinum foil, and heated gently in a quartz tube attached to the bottling apparatus. A removable mica sleeve wound with a thin ribbon of a commercial high-melting alloy furnished the necessary heat, with the help of a moderate electric current. After completing the dehydration, the platinum foil was removed and the boat and contents were heated for several hours at a gradually increasing temperature until the salt just fused, pure carbon dioxide being passed through the tube. As soon as fusion had taken place, the application of heat ceased and pure air was admitted, gradually decreasing the amount of carbon dioxide until, when the boat was cold, pure air was passing over it. The weight obtained this way was constant after successive trials, which was not the case when the salt was fused in nitrogen or air, a slight gain in weight being usually noted in the latter case. In the presence of air, at about 850°, fused sodium carbonate attacks platinum to a slight extent, especially if the salt is kept fused for a considerable time. Hoping to avoid this difficulty,

¹ Richards and Cox, *THIS JOURNAL*, 36, 819 (1914).

² Richards, Faraday Lect., *J. Chem. Soc.*, 99, 1203 (1911). See Richards and Parker, *Proc. Acad. Arts and Sciences*, 13, 86 (1897).

we used a gold boat in preliminary work, but this steadily gained in weight even after 60 hrs. treatment with nitric acid and prolonged ignition in air. Returning to the platinum boat, we found that in a stream of pure carbon dioxide free from air it was possible, by very gradually increasing the temperature until the salt was just fused, to prevent any significant action on the platinum boat. Thirteen fusions decreased the weight of the boat only 0.27 mg., or 0.02 mg. during each fusion.

There is reason to believe that sodium carbonate thus fused in a stream of pure carbon dioxide is purer than sodium carbonate prepared in any other way. The cooled mass could have contained no excess of carbon dioxide, since the vapor pressure of this gas from the bicarbonate at the temperature employed is enormous; moreover, because the salt came to constant weight on successive fusions, there is no suspicion of abnormal loss of carbon dioxide. Because we have been able to find no record of anyone's having prepared the salt in this way before, these samples were perhaps the purest specimens of it which have ever been made. Our experience shows that sodium carbonate, as ordinarily prepared for quantitative work, is not perfectly dry. Material heated at dull redness for a short time, as usual in most laboratories, was found to lose on fusion sometimes as much as 0.05% of moisture; and even after two hours of such heating the loss was about 0.03%. Material heated for a long time just below the fusion point lost on fusion only about 0.003%. The losses during our experiments ranged between these limits. It is true that for ordinary work such errors are immaterial; but in the most accurate work they become highly important.

The Solution and Quantitative Neutralization of the Sodium Carbonate.

Having been carefully weighed in the weighing bottle containing dry air, into which it was transferred in the bottling apparatus, the sodium carbonate was now dissolved and neutralized in pure, dilute hydrobromic acid. This solution was provided in carefully weighed quantity almost exactly necessary to neutralize about 5 g. of sodium carbonate, the amount usually employed in a determination. Because the method of dealing with this standard acid solution was somewhat unusual, a brief description is fitting.

Specially designed weighing burets containing the desired quantity of acid solution (about 200 cc.) were employed to weigh it. A large amount of the solution had been prepared shortly beforehand, and preserved in a bottle of resistant glass, from which it could be removed by a paraffin-coated and -lined glass syphon. Air was admitted to the bottle after passing through a U-tube containing a solution of the same nature and concentration as that in the bottle. When the buret was to be filled, after thorough agitation of the solution (which was at room temperature) a portion was drawn off sufficient to wash the interior of the syphon—

the last of this being added to the U-tube, replacing the solution which had previously been in the tube. Small portions of the acid solution were now run into the dry weighing buret, which was closed and gently shaken until it was thoroughly rinsed and filled with the vapor of the solution. The buret was then filled, with the syphon-tip inserted far into its interior, to avoid evaporation. Subsequently, the buret was carefully wiped with a slightly damp, perfectly clean linen cloth, and thereafter touched only with platinum forceps or linen cloth. After standing with the upper cock nearly closed in the balance case for one hour, the weight was taken by substitution, using a precisely similar, partly filled companion buret as substituting tare. Before filling a buret, the bottle containing the acid solution had been placed for some hours near the balance so that long waiting was unnecessary.

The required amount of solution was next removed from the buret and placed in the bowl of a very large platinum retort, the graduations upon the buret allowing one to determine to within 0.1 g. when the required weight had been removed. The buret was then returned to the balance case and in not less than an hour its weight was determined as before. It was found that three such complete manipulations could be carried out in succession; each consisting of weighing after one hour in the balance case, removing buret to the titration-room, replacing and removing the tip from the buret outlet, and reweighing, without any change in weight exceeding a milligram. As a rule, of course, in actual analysis, only one such operation was carried out.

As will be detailed, the concentration of this solution was exactly determined by reference to silver—the solution being weighed out for this purpose in successive portions just as for the neutralization; but, in order to not interrupt the narrative, the discussion of the neutralization will be continued.

As already stated, the exactly weighed acid solution was placed for the neutralization of the sodium carbonate into the body of a large platinum retort, very kindly given by Professor J. M. Crafts; and the weighed boat with the fused carbonate was carefully lowered into the solution. The tightly fitting cover was then placed on the retort, with the condenser tube attached; and the whole was set aside for some hours, usually over night. The condenser tube was packed with scraps of platinum foil to serve as baffles, and the lower end placed into a gold flask which served to collect any solution projected in minute drops during the evolution of gas. When the fused salt was completely dissolved, the retort with condenser attached was very gradually warmed during several hours until at last boiling commenced. The supply of heat was then decreased and the condenser tube and gold flask were removed and rinsed into the retort, which was now covered, placed in an electric oven or bath, and warmed

while very pure air was passed in through a hard glass tube bent to deliver the air just above the surface of the liquid. During the evaporation thus conducted, the temperature of the oven was maintained at a point slightly above 100° , actual ebullition being prevented by the cooling effect of rapid vaporization. When the volume of the solution had been reduced to about one-half, the heating was discontinued, and the retort was cooled in a current of pure air. Methyl red was added to the cool liquid as indicator, showing in general an alkaline reaction; this outcome had been arranged beforehand in weighing the acid, in order to prevent possible loss of bromine during the evaporation.

The next step was the completion of the titration, using a very dilute solution (approximately $0.01\ N$) of hydrobromic acid, which had been prepared by diluting the more concentrated acid and standardized by titration against dilute carbonate-free sodium hydroxide and by precipitating with silver nitrate. This dilute standard solution was weighed in a smaller set of weighing burets, and added drop by drop to the solution in the retort. For this purpose, the platinum cover of the retort had been removed and a glass plate having two small openings put in its place; through one of these openings the tube admitting a rapid stream of pure air was passed, while the other served to admit the tip of the weighing buret. When a distinct acid reaction was attained, the buret was removed; and if the amount added was comparatively large the buret was weighed and emptied. If, however, the amount added was small, the buret was placed in the balance case and removed for a second addition after the carbonic acid formed by the previous addition had been expelled. As with the stronger solution, we found that it was possible, using care not to touch the buret with the hands and allowing but little change in the temperature of the room, to work with the buret for several hours without producing a significant change in the weight.

The expelling of the carbon dioxide produced by the addition of dilute acid was usually complete within one-half hour at a temperature just below boiling, with a rapid current of pure air passing over the solution. In no case was there a change in the depth of indicator color after the solution had been heated for one hour. Consequently, this was the usual time of heating the retort, after the addition of a portion of dilute acid. Experience taught that a certain depth of pink was required in order that the solution would be left neutral when the excess of carbonic acid had been expelled, and this helped materially to shorten the tedious process of reaching the end point by this method. In short, this method of adding successive small portions of very dilute hydrobromic acid was continued until an end point slightly on the acid side of exact neutrality was reached, which remained unchanged when cold, after at least an hour's heating, entirely with slight boiling during the last stage. It was thought

for a time in the preliminary work that the end point might be determined in a hot solution; but the action of the indicator is less reliable at the higher temperature under the conditions concerned; and the difficulty of manipulating the hot solution, especially because of the obstruction of clear vision by the drops condensed on the glass plate, caused us to cool the liquid in order to attain the accuracy demanded.

In two titrations an equivalent amount of *p*-nitrophenol was added to the methyl red. This mixture is very well adapted for the titration of all strong acids and bases, working from either acid or alkaline solution. With a concentration of ionized hydrogen of 10^{-8} , the mixture shows a distinct yellow color, at 10^{-7} the color is a very faint greenish yellow, almost colorless, while at 10^{-6} the pink of methyl red appears. In hot solution it is less reliable than methyl red alone, tending to make the solution appear too alkaline; but it resumes its normal reaction when cooled to room temperature. It cannot be depended upon in solutions containing more than 15 or 20% of dissolved substance, especially in sulfate solutions. The weight of the indicator substance required is very small; from 0.05 to 0.08 mg. of methyl red sufficing for 100 cc. solution;—and the amount transformed, when a distinct pink is noticed, is not more than one-half this, as determined by Noyes's method of superimposing solutions. Hence, considering the high molecular weight of the indicator, it is certain that no weighable amount of acid or base was required to combine with the indicator. Confirming this conclusion, it was found that one drop of 0.01 *N* solution of acid containing 0.03 mg. of bromine would change the reaction from distinct alkaline to distinct acid. For yellow or red indicators the eye is much more sensitive to a small change in color when the solution is placed in the bottom of a platinum vessel than when it is contained in glass or porcelain. The methyl red, of course, gives the final evidence as to the true neutral point, but for rapid work the mixture of indicators can be used to advantage, since it gives more warning of approach to the end point from either acid or basic side.

After the sodium carbonate had been neutralized with hydrobromic acid, the sodium bromide solution resulting was quantitatively transferred to a glass-stoppered precipitating flask, and diluted; and the calculated quantity of silver, having been dissolved with great precaution in nitric acid, was added. The exact end point of the precipitation was determined in the usual nephelometric manner.

The above-described method of reaching the end point by gradual addition of very dilute hydrobromic acid was employed in five of the six determinations. In the third experiment (No. 11 in the second table below) a very slight excess of hydrobromic acid was added during the first operation. This excess was titrated very carefully with dilute, carbonate-free sodium hydroxide solution which had been standardized

against both dilute and concentrated hydrobromic acid solutions. The fact that in this experiment essentially the same quantity of hydrobromic acid was used as in the others, suggests that the danger of loss of bromine during evaporation from an acidifying liquid is very slight.

Besides thus finding the weight of silver needed to precipitate the ionized bromine balancing the ionized sodium from the sodium carbonate, we made separate determinations of the amount of silver needed to precipitate given weights of the same solution of hydrobromic acid, and also in four cases weighed the silver bromide which resulted. By giving the exact weights of silver and of bromine corresponding to a given weight of the hydrobromic acid solution, these determinations made it possible to compute (in a way entirely independent of the other determinations) the amount of silver and silver bromide corresponding to given weights of the solution used for neutralizing various portions of sodium carbonate—it being assumed, of course, that the neutralization was correctly performed. The agreement of these results with the others showed that, at least as far as the determination of the bromine was concerned, the earlier results were trustworthy. They showed, moreover, that no significant amount of hydrobromic acid was lost, on the average, during neutralization and evaporation, for the silver analyses were made in one case after evaporation and in the other, case without any such treatment. Several of these analyses were made in the midst of the earlier series; indeed, the intention was to make them alternately.

The question having arisen as to the possible action of the dilute hydrobromic acid on the resistant bottle in which it was kept, experiments were instituted on purpose to test this point; for such action would have had a highly deleterious effect upon the result, introducing sodium bromide from a foreign source. The final distillation of the acid had occurred on March 20, 1913, and not long afterwards the solution was made up in its final form. All the analyses were concluded before the 10th of May, an interval of less than seven weeks. Six months after that, the acid having remained in the same bottle, two portions of 60 g. each were separately evaporated in a quartz dish, and the barely visible trace of residue was dissolved in water, transferred to a small platinum crucible, dried and weighed. In each case the residue weighed only 0.1 mg., and the solution in water was found in the nephelometer to contain an amount of soluble bromide equivalent to 0.04 mg. sodium bromide. The amount of sodium bromide formed from the flask during the first six weeks in question must, therefore, have amounted to less than 0.01 mg., a negligible quantity. It should be stated that this flask had previously been used for dilute hydrobromic acid for several years; probably a new bottle would not have yielded so satisfactory a result.

Incidentally, in order to reduce the results to the vacuum standard,

the specific gravity of sodium carbonate was determined by weighing it in a pycnometer, under toluene which had been found in two closely agreeing experiments to have a density at 20° of 0.8661 referred to water at 4°. Thus 9.7256 g. and 5.62691 g. of salt were found to displace 3.32581 g. and 1.92439 g. of toluene, respectively, at the same temperature. The two values for the density of the salt were, therefore, 2.5327 and 2.5325, respectively. This value is distinctly higher than the results of other experimenters. For example, Schroeder found values ranging between 2.43 and 2.51.¹ The difference is doubtless due to the more compact condition of our fused material, and the absence of air held within the pores of the substance.

The first of the tables below reports the weights of silver and silver bromide obtained from given weights of the standard hydrobromic acid solution. All the analyses are recorded, excepting two which met with accidents and could not be brought to completion.

TABLE I.—ANALYSES OF HYDROBROMIC ACID SOLUTION.

| No. of expt. | Sample of silver. | Wt. HBr sol (in vac.). | Wt. Ag (in vac.). | Wt. AgBr (in vac.). | Wt Ag per 100.000 g. solution. | Wt. AgBr per 100.000 g. solution. |
|-----------------|----------------------|---------------------------|----------------------|------------------------|--------------------------------------|---|
| 1..... | | 205.192 | | 17.05459 | ... | 8.3115 |
| 2..... | | 199.157 | | 16.55319 | ... | 8.3116 |
| 3..... | I | 212.457 | 10.14346 | 17.65772 | 4.7743 | 8.3112 |
| 4..... | II | 211.335 | 10.08975 | 17.56405 | 4.7742 | 8.3111 |
| 6..... | III | 201.663 | 9.62812 | | 4.7744 | ... |
| 8..... | II | 198.356 | 9.47115 | | 4.7748 | ... |
| Average..... | | | | | 4.77442 | 8.31135 |

Thus 100.000 g. of silver bromide are found (from the two averages) to correspond to 57.4446 g. of silver. Baxter² found 57.4453 g.—very nearly the same figure. If we assume Baxter's value (because determined in a simpler way) to be correct, our average, 4.77442 g. of silver, corresponds to 8.31125 g. of silver bromide, or very nearly the result 8.31135 found directly, as given above. The average between these averages, or 8.31130 g. of silver bromide, must represent very nearly the true amount of precipitated halide to be obtained from 100.000 g. of the hydrobromic acid solution. This weight of silver bromide corresponds to 3.5815 g. of hydrobromic acid gas—a figure which gives the percentage composition of the acid, enabling us to know the density of the solution and apply accurately the large correction to the vacuum standard in weighing.

Evidently the concentration of the hydrobromic acid remained essentially constant during the time concerned.

The second table, below, records the weights of hydrobromic acid solution taken for the neutralization of the several samples of sodium car-

¹ Landolt-Börnstein, p. 180 (1912).

² *Proc. Am. Acad.*, 42, 210 (1906).

bonate, the weights of these samples, the weights of the salt corresponding to 100.000 g. of acid solution, and finally the molecular weight of sodium carbonate and the atomic weight of carbon computed from these results (with the help of the weight of silver bromide corresponding to the hydrobromic acid as computed from Table I) if silver is 107.88, bromine 79.916, and sodium 22.995. Incidentally, the total weight of the dilute acid would have been capable of precipitating $1254.946 \times 0.083113 = 104.3023$ g. of silver bromide, hence we may write the proportion:— $104.3023 : 29.43501 = 2 \times 187.796 : 105.995 = \text{Na}_2\text{CO}_3$.

TABLE II.—MOLECULAR WEIGHT OF SODIUM CARBONATE, FIRST METHOD.

| No. of expt. | Wt. of HBr sol. (in vac.). | Wt. of Na_2CO_3 (in vac.). | Wt. of Na_2CO_3 per 100.000 g. solution. | Calc. mol. wt. Na_2CO_3 (if AgBr = 187.796). | Calc. at. wt. carbon (if Na = 22.995). |
|--------------|----------------------------|--|--|--|--|
| 9..... | 202.744 | 4.75555 | 2.34559 | 105.998 | 12.008 |
| 10..... | 204.673 | 4.80081 | 2.34560 | 105.999 | 12.009 |
| 11..... | 208.457 | 4.88936 | 2.34550 | 105.994 | 12.004 |
| 12..... | 240.119 | 5.63157 | 2.34533 | 105.987 | 11.997 |
| 13..... | 191.646 | 4.49516 | 2.34555 | 105.996 | 12.006 |
| 14..... | 207.307 | 4.86256 | 2.34559 | 105.998 | 12.008 |
| Sum, | 1254.946 | 29.43501 | Av., 2.34553 | 105.995 | 12.005 |

The average value for carbon is seen to be 12.005. Considering the circumstances, the agreement of the individual results is as good as could be expected. Before discussing the outcome, another series of more directly obtainable data (namely, the weights of silver actually needed for the precipitation of the exactly neutralized sodium bromide made from these specimens of sodium carbonate) will be recorded. In Table III these several weights of silver are entered in the fifth column (the quality of the silver being indicated by the numerals in the third, which correspond to the various samples already described). The next to the last column, again, contains the computed molecular weight of sodium carbonate, and the last column the atomic weight of carbon, calculated on the same basis as the values recorded in Table II.

TABLE III.—MOLECULAR WEIGHT OF SODIUM CARBONATE, SECOND METHOD.
BY MORE DIRECT REFERENCE TO SILVER.

| No. of expt. | Sample of Na_2CO_3 . | Sample Ag. | Wt. of Na_2CO_3 (in vac.). | Wt. of Ag (in vac.). | Mol. wt. Na_2CO_3 if Ag = 107.88. | At. wt. carbon if Na = 22.995. |
|--------------|--------------------------------------|------------|--|----------------------|---|--------------------------------|
| 15..... | (A) | I | 4.75555 | 9.68023 | 105.995 | 12.005 |
| 16..... | (A) | II | 4.80081 | 9.77222 | 105.997 | 12.007 |
| 17..... | (B) | II | 4.88936 | 9.95301 | 105.991 | 12.001 |
| 18..... | (B) | III | 5.63157 | 11.46316 | 105.998 | 12.008 |
| 19..... | (C) | III | 4.49516 | 9.15003 | 105.997 | 12.007 |
| 20..... | (C) | II | 4.86256 | 9.89811 | 105.994 | 12.004 |
| Sum, | | | 29.43501 | 59.91676 | Av., 105.995 | 12.005 |

In brief, it appears that the atomic weight of carbon calculated from the weight of hydrobromic acid taken is exactly identical with that found from the directly determined weight of silver needed to precipitate the acid required for neutralizing the carbonate, each being 12.005 on the basis given, if silver equals 107.88. On the other hand, if $Ag = 107.871$ (a contingency not impossible), carbon becomes exactly 12.000. The probable error of the average of the entire series of twelve values, if each is given equal weight, is less than 0.001 in the atomic weight of carbon. This is less than 0.003% in the weight of the sodium carbonate, or less than 0.2 mg. in the actual weighing of this salt. The results then are about of the order of accuracy of much of the modern careful work on atomic weights.

The final limits for carbon, *viz.*, 12.000 to 12.005, according to the value for silver chosen, are near that found for carbon in other ways. The range is indeed, as small as the limit of accuracy of the usually accepted data concerning either carbon or silver. That in this entirely different way the old value for carbon should be verified is a highly comforting and reassuring circumstance. It inspires confidence in the accuracy of all the processes concerned, both in the new work on halogen compounds and the older work on carbon; because the single method may be always open to the suspicion that a small constant source of error may have been inadvertently overlooked, the value of such confirmatory evidence is great.

The work could not have been carried out at this time without a generous subsidy from the Carnegie Institution of Washington, which is hereby gratefully acknowledged.

Summary.

A new method of determining the molecular weight of sodium carbonate, and therefore, the atomic weight of carbon, is described, depending upon the neutralization of pure, fused, weighed sodium carbonate by hydrobromic acid, and the precipitation of the bromine both in the resulting sodium bromide and other portions of original solution by means of pure silver. It was found that 29.43501 g. of sodium carbonate were equivalent to 59.91676 g. of silver, and also to a weight of dilute hydrobromic acid which had been found in other tests to be capable of precipitating 104.3023 g. of silver bromide. From these results, if silver equals 107.88, sodium carbonate becomes 105.995 and carbon 12.005, and if silver equals 108.87 and sodium 22.993, carbon becomes 12.000. These limits in both cases are about the possible range of accuracy of the earlier determinations by various methods. Hence the present work, by connecting the various ratios in a new way, shows the consistency of a great variety of earlier work.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD COLLEGE.]

THE MOLECULAR WEIGHT OF SODIUM SULFATE AND THE ATOMIC WEIGHT OF SULFUR.

By THEODORE WILLIAM RICHARDS AND CHARLES R. HOOVER.

Received November 19, 1914.

The preparation and neutralization of pure sodium carbonate, for which the way had been cleared by the work described in the foregoing paper, provides a standard of reference for many other precise determinations. The present paper discusses briefly a series of determinations of the ratio between sodium carbonate thus prepared and sodium sulfate made from it by exact neutralization with sulfuric acid. This comparison had already been attempted long ago by one of the authors.¹ The old determinations were, however, made only as a side issue in the course of an extensive study of the atomic weight of copper; they showed a rather large range of error, and were made with sodium carbonate which was then known to contain traces of silica;² moreover, our recent work on the fusion of sodium carbonate showed that this older specimen, merely dried at a dull red heat, must have contained traces of water also. Therefore, it seemed well worth while to repeat the experiments with modern precision.

The program here was simpler than that involved in the immediately preceding research on carbon. The fused sodium carbonate was carefully weighed, and treated in the platinum retort with a very slight excess of pure sulfuric acid; the solution was then freed from carbon dioxide and evaporated quantitatively in a quartz flask without boiling, but with the help of a current of air; and the remaining salt was fused and weighed.

Preparation of Materials.

Most of the materials were prepared just as before, the same three samples of sodium carbonate being employed. The sulfuric acid was made from the purest acid of commerce (which contained only minute traces of impurity) by three successive distillations in a non-tubulated glass retort over a ring burner. Only the middle portions of each distillate were used. Among other substances sought in this acid was selenium, which was tested for in a 20 cc. portion of the original substance by dilution with twice its volume of water, treatment with half its volume of concentrated hydrochloric acid after cooling and then boiling until the mixture occupied about 35 cc. No free chlorine was detected during this process, and the solution upon treatment with sulfur dioxide showed no red coloration. This test is supposed to show 0.003% of selenium; therefore, presumably, this element was absent. The quantitative outcome to be given later certainly indicates that no element with a greater atomic weight than sulfur was present, confirming the qualitative test.

¹ *Proc. Am. Acad.*, 26, 268 (1891); *Z. anorg. Chem.*, 1, 180 (1892).

² *Ibid.*, 247 and 157, respectively.

The pure redistilled acid was diluted with pure water to a convenient standard concentration, suited to the capacity of the weighing buret and the amount of carbonate to be neutralized.

The preliminary standardization of the standard solution of acid was carried out as follows, much more simply than in the final experiments. This simple preliminary procedure is within the scope of the apparatus in any laboratory, and may be useful to those wishing to standardize an acid solution. A quantity of air-dehydrated, thrice recrystallized sodium carbonate was placed in a weighed platinum crucible. This was heated on a pipe stem triangle while dry carbon dioxide was passed in through a Rose crucible lid, the usual porcelain delivery tube having been replaced by a slightly longer, hard-glass tube. After having been kept at a temperature below fusion for some time, the salt was carefully fused and kept in a liquid condition for a few minutes. It was then cooled in a current of carbon dioxide and weighed again. The crucible and contents were placed in a weighed quantity of the standard solution of sulfuric acid known to be insufficient to neutralize all the carbonate, and the liquid was heated nearly to boiling after the addition of the mixed indicator. When the acid had been exhausted, the effervescence naturally ceased, and the solution of the carbonate proceeded very slowly; therefore, it could be easily determined when more acid was needed. Adding acid drop by drop, from time to time, the carbonate was finally dissolved and the solution remained neutral. The process may, of course, be conducted with even less trouble by adding at first a slight excess of acid and titrating back with hydroxide. By this crude method 1 g. of sodium carbonate was found to be equivalent to 41.032 g. of acid solution, while in the more carefully executed titration in the first regular analysis, 1 g. of pure sodium carbonate was found to be equivalent to 41.0280, or a difference of 1 part in 10,000. This is a degree of accuracy far exceeding that possible by the ordinary methods used for the volumetric neutralization of sodium carbonate, which gives rather questionable results in inexperienced hands.¹ The standard acid evidently contained 2.255% of H_2SO_4 .

An auxiliary solution, 100 times less concentrated, was next prepared by diluting a weighed amount of the main standard solution with a weighed amount of water. These solutions were kept in resistant glass bottles with paraffin-covered rubber stoppers and paraffin-coated syphon tubes. Air was admitted through large U-tubes filled with beads and with portions of solution removed from time to time from the bottles. That a dilute solution may be preserved without appreciable change in concentration, was shown by the results of the titration of hydrobromic acid against sodium carbonate described in the previous paper.

¹ The uncertainty due to the indicator alone may amount to as much as 0.5% in the presence of carbonic acid. See A. A. Noyes, *THIS JOURNAL*, 32, 815 (1910).

The Neutralization and Determination.

The exact titration of accurately weighed amounts of the purest fused carbonate against sulfuric acid was carried out essentially as in the case of the hydrobromic acid. The end point chosen was slightly more on the acid side of exact neutrality, the hydrogen ion concentration being about 10^{-6} , because the excess of acid could be driven off during the subsequent ignition. The non-volatility of sulfuric acid from aqueous solution allowed more variation in the method of reaching the end point than in the earlier case. The quantity of the main sulfuric acid solution required to combine with the observed weight of sodium carbonate was weighed out, and the carbonate was dissolved in the acid in the platinum retort. In determinations 2, 3, and 6 the neutral point was reached by several further very small additions of very dilute acid, as in the earlier case. In Nos. 4 and 5 a slight excess of sulfuric acid was added in the first operation, and the solution was titrated back with standard sodium hydroxide solution from a weighing buret. In No. 1 a very slight excess of acid added was removed by repeated evaporation and ignition of the sodium sulfate to constant weight, followed by thorough fusion in a rapid current of air. These different methods of treatment, by substantially agreeing as to their results, established the fact that the carbon dioxide had been completely expelled from the solution when the end point was reached in the hydrobromic acid analysis described in the preceding paper.

After the solution of sodium sulfate had been rendered neutral or slightly acid, it was concentrated by passing pure air over the solution in the covered platinum retort until the volume indicated that the solution would be slightly more than saturated at room temperature. It was then transferred, while warm, to a small quartz flask in which it was to be evaporated and fused somewhat in the manner employed in a previous research upon silver nitrate.¹ In the present case, however, the flask had the tube for admitting the air fused into the top of the flask, and a side exit tube attached after the fashion of a gas washing bottle. Both tubes were provided with ground quartz stoppers. The flask had a capacity of about 100 cc. and was not too large to weigh accurately. The transference from the retort to this flask was naturally the most delicate part of the work. By placing a curved glass rod within the retort with the curve emerging tangent to the inner edge, but free from the outside portion of the rim, it was possible to pour the solution from the retort along the rod without danger of loss. A small funnel tube drawn out and bent slightly at its extremity guided the stream well down into the inlet tube of the quartz flask, and the transfer was facilitated by clamping the flask in an inclined position. The flask having been filled to within a short distance below the end of

¹ Richards and Forbes, Carnegie Inst. Wash., Publication 69, 51 (1907). *THIS JOURNAL*, 29, 808 (1907).

the inlet tube, was placed in an electric heater, maintained at a temperature just insufficient to cause ebullition—pure air being passed in through a glass tube ground to fit the quartz inlet tube. The retort cover and condenser were then thoroughly rinsed, and the solution with several wash waters placed in the platinum retort and concentrated to small bulk; then the solution was added to the contents of the quartz flask. Generally, three such series of washings were carried out until it was certain that every weighable trace of salt had been transferred. After the sodium sulfate solution had been completely collected in the quartz flask and dried, the large electric oven (which had completely enclosed the flask) was exchanged for another consisting of a fire-clay tube wound for a higher temperature, and large enough to enclose only the bulb. With this heater a temperature just sufficient to fuse the edges of the mass of sulfate was maintained for several hours, after which the temperature was raised for a short time to the point necessary to fuse the salt (about 875°). A current of pure air was passed through the flask throughout all these steps. It was found that two hours' heating at the lower temperature (about 850°) produced constant weight, and that on fusion only a very small apparent loss in weight appeared, the average in five trial determinations being 0.01 mg. per gram of salt. This absence of a decrease in weight shows that very little water was retained within the porous, brittle solid at this high temperature. The final calculation was, of course, made on the basis of the weight of salt after fusion, and for the purpose of correcting this weight to the vacuum standard, the density of fused sodium sulfate (previously unknown) was determined as follows: 6.07615 and 8.43725 g. of salt (*in vacuo*) displaced 1.9519 and 2.7063 g. (*in vacuo*) of toluene, respectively, the toluene having a density of 0.8661 at 20° . The two determinations yielded as results 2.696 and 2.700 for the density, respectively—or in the mean, 2.698.

The weighing of vessels of quartz or glass as large as the flasks and burets used in this work is accompanied always by some difficulty; but if the vessels are provided with precisely similar counterpoises and if each piece of apparatus is kept in a separate desiccator and each weighed under precisely the same conditions after the same time, good results may be obtained. In this work, of course, the weights were carefully standardized, the counterpoises were made of volume and weight like those of the objects to be weighed, the weighing room was carefully guarded as to constancy of temperature, corrections for changes of pressure were applied when needed, and the customary details necessary for accuracy were faithfully heeded. The keeping of the small tube of radioactive material in the balance case greatly helps in the discharge of electrical charges—always so troublesome with large nonconducting vessels. The ideal laboratory conditions possible in the new laboratory, built especially for

this kind of work, greatly facilitated the convenience of the task and accuracy of the outcome. The results of the comparison of sodium carbonate with sodium sulfate are given in Table I. In the first column is given the number of the experiment; in the second, the sample of sodium carbonate; in the third, the weight of sodium carbonate *in vacuo*; in the fourth, the weight of sodium sulfate; in the fifth, the weight of this latter salt corresponding to one gram of sodium carbonate; and in the last column, the atomic weight of sulfur—assuming that the molecular weight of sodium carbonate is 105.995, sodium being 22.995 and carbon 12.005, as found in the preceding investigation. The maximum deviation from the mean is less than 0.003% of the molecular weight of the sodium sulfate, and the "probable error" of the average value is less than 0.001.

TABLE I.—THE RATIO BETWEEN SODIUM CARBONATE AND SODIUM SULFATE.

| No. of Expt. | Sample of Na ₂ CO ₃ . | Wt. fused Na ₂ CO ₃ (<i>in vac.</i>). Grams. | Wt. fused Na ₂ SO ₄ (<i>in vac.</i>). Grams. | Wt. of Na ₂ SO ₄ from 1.000,00 g. Na ₂ CO ₃ . | At. wt. sulfur. |
|--------------|--|---|---|--|--------------------|
| 1..... | A | 5.25191 | 7.03829 | 1.34014 | 32.058 |
| 2..... | B | 4.50977 | 6.04382 | 1.34016 | 32.060 |
| 3..... | B | 5.04233 | 6.75737 | 1.34013 | 32.057 |
| 4..... | B | 3.67340 | 4.92304 | 1.34019 | 32.063 |
| 5..... | C | 4.18724 | 5.61151 | 1.34015 | 32.059 |
| 6..... | C | 4.55100 | 6.09916 | 1.34018 | 32.062 |
| Sum, | | 27.21565 | 36.47319 | Av., 1.340155 | 32.060 |

Thus it is clear that 1.00000 part of sodium carbonate is equivalent to 1.340155 parts of sulfate; hence, if silver is taken as 107.88 and sodium carbonate as 105.995, Na₂SO₄ = 142.050 and sulfur is found to be 32.060. This figure is only a little below the value 32.069 found at Harvard eight years ago by a more direct method—the conversion of silver sulfate into the chloride.¹ The substantial agreement of the results affords good evidence that the roundabout comparison adopted in the present research is trustworthy in each of its varied steps, and incidentally confirms the value for carbon given by the foregoing research. Evidently we cannot be far wrong in assuming that the correct value for the atomic weight of sulfur is the mean between the two results—that is to say, 32.065. If silver is taken as 107.871 (instead of 107.88) this value becomes 32.056.

The comparison of the ratio of sodium carbonate to sodium sulfate with the old results of 1891 is not without interest. The average of all the old results² made the ratio 1.0000 : 1.3399, while the average of the last three most trustworthy results made it 1.0000 : 1.3400 (instead of the new value 1.340155). The respective errors of the older averages were thus 0.022 and 0.011%. Errors of this sort are precisely of the order

¹ Richards and Grinnell Jones, *Pub. Carnegie Inst. Washington*, 69, 69 (1907); *THIS JOURNAL*, 28, 826 (1907).

² *Loc. cit.*

caused by the retention of water in the unfused sodium carbonate employed in the early work—and there can be little question that this substance must have really contained in 1891 at least as much water as we found it to contain in 1913, under similar circumstances.¹ The sodium sulfate had been fused, then as now. Hence the atomic weight of copper as found in 1891 by comparison with sodium carbonate must have been lower than the truth by perhaps 0.022. Correcting, we find the recalculated atomic weight of copper to be 63.554 (instead of 63.532²) a value much more nearly agreeing with that found from the direct comparison with silver, namely, 63.57.

This investigation, like the foregoing, was conducted under the favoring auspices of the Carnegie Institution of Washington.

Summary.

The quantitative conversion of pure fused sodium carbonate into pure sodium sulfate is described, the ratio of the equivalent weights of these substances being found to be 1.00000 : 1.340155. Assuming $\text{Na}_2\text{CO}_3 = 105.995$, as found in the preceding research ($\text{Ag} = 107.880$), the molecular weight of sodium sulfate becomes 142.050, and the atomic weight of sulfur becomes 32.060. This is in reasonable agreement with the earlier Harvard value, 32.069, and the mean of the two, 32.065, may perhaps be taken with some confidence as the most trustworthy value thus far recorded. This research, like that immediately preceding it, has been useful in confirming by cross-reference many varied methods and results, and in eliminating slight apparent inconsistencies in earlier results; and the out-come seems to strengthen our confidence in the processes upon which our present table of atomic weights is founded.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF CADMIUM.

[THIRD PAPER.]

THE ELECTROLYTIC DETERMINATION OF CADMIUM IN CADMIUM CHLORIDE.

BY GREGORY PAUL BAXTER AND MINNIE LOUIS HARTMANN.

Received November 14, 1914.

In three recent papers dealing with the atomic weight of cadmium, Hulett and his collaborators at Princeton University have obtained concordant results, which indicate that the atomic weight of cadmium

¹ See page 100 of preceding article.

² This recalculation is of the figures on the top of p. 271, *Proc. Am. Acad.*, 26 (1891). Na_2CO_3 is assumed as 105.995 above, instead of as 106.108, as it was twenty years ago.

is 112.3, a value one-tenth of a unit lower than that obtained in the Harvard Chemical Laboratory some years ago. Perdue and Hulett,¹ by the electrolytic determination in a mercury cathode of the cadmium in both the hydrated and anhydrous sulfate, and by the determination of the water in the hydrated sulfate, found the atomic weight of cadmium to be 112.30. Laird and Hulett² simultaneously deposited silver and cadmium electrolytically, the latter in a mercury cathode. From the relation of the weights of the two metals deposited, they compute the atomic weight of cadmium to be 112.31 ($\text{Ag} = 107.88$). Very recently Quinn and Hulett³ have determined by electrolytic deposition in a mercury cathode the cadmium content of anhydrous cadmium chloride and bromide. The atomic weight of cadmium found in this way is 112.3 ($\text{Cl} = 35.458$, $\text{Br} = 79.92$). Thus the three investigations support one another in a striking way.

On the other hand, Baxter and Hines⁴ analyzed anhydrous cadmium chloride, by comparison with pure metallic silver and by weighing the silver chloride formed, with the average result for the atomic weight of cadmium of 112.417, while a little later Baxter, Hines and Frevert⁵ repeated this work on cadmium chloride with the result 112.418. The latter investigators also analyzed anhydrous cadmium bromide in a similar fashion, and obtained the identical value 112.417.

Such a serious discrepancy is very disturbing, since it points to some fundamental difficulty with either the electrolytic determination of metals in a mercury cathode or with the analysis of metallic halides by the "silver" method. In the determination of the cadmium in cadmium chloride, the discrepancy amounts to 0.0004 g. of metal in every gram of chloride, while one gram of cadmium chloride would yield 0.0010 g. less silver chloride if the atomic weight of cadmium has the higher rather than the lower value. Since in all the investigations referred to several grams of material were used in each experiment, the uncertainty is obviously far greater than any ordinary experimental error.

The "silver" method of analysis of metallic halides has already been subjected to prolonged and searching investigation, and has been found to yield results in very satisfactory agreement with those obtained by radically different methods.⁶ Furthermore, in the investigations upon the cadmium halides in this laboratory, no especial difficulties were encountered. The silver halides were found to be free from occluded material, both by direct analysis and by the comparison of the quantity of silver used with

¹ *J. Phys. Chem.*, **15**, 1579 (1911).

² *Trans. Am. Elec. Soc.*, **22**, 385 (1913).

³ *J. Phys. Chem.*, **17**, 780 (1913).

⁴ *THIS JOURNAL*, **27**, 222 (1905); *Z. anorg. Chem.*, **44**, 158.

⁵ *Ibid.*, **28**, 770 (1906); **49**, 415.

⁶ Cf. Richards and Archibald, *Proc. Amer. Acad.*, **38**, 443; Baxter, Thorvaldson and Cobb, *THIS JOURNAL*, **33**, 319 (1911); Baxter and Hoover, *Ibid.*, **34**, 1657 (1913).

the weight of silver halide produced in each experiment. Furthermore, there was no evidence of basicity in the salts which had been made anhydrous by fusion in an acid atmosphere, and the fact that both chloride and bromide yielded identical results made it improbable that either retained moisture during fusion. We decided, therefore, to repeat a portion of the work of the Princeton investigators, by determining electrolytically the cadmium content of the anhydrous chloride. Neither of the other methods used by Hulett and his collaborators seemed as promising as this one, for, as Richards¹ has already pointed out, hydrated crystals are likely to contain an excess of included or *dissolved* water, while it is not easy to obtain in a coulometer silver deposits in which the proportion of occlusions is known. Both of these difficulties would tend to *lower* the observed atomic weight of cadmium.

The results of this research have been satisfactory beyond our anticipation in the exactness with which they support the earlier Harvard work, for if one adds to the percentage of chloride found by Baxter, Hines and Frevert the percentage of cadmium found here, the sum is exactly one hundred per cent. within the limit of experimental error.

In the analysis of cadmium chloride and bromide, Quinn and Hulett converted weighed amounts of anhydrous salt to sulfate and deposited the cadmium electrolytically in a mercury cathode contained in an amalgamated platinum cup. Our method was simpler and safer, in that the cadmium chloride was not converted to sulfate, but was electrolyzed directly. The greater portion of the chlorine is freed as such at the anode, and, while a small amount of perchloric acid which is formed, remains, this is far less hindrance to the complete deposition of the metal than the relatively large amount of sulfuric acid which results from electrolysis of the sulfate. Even under these conditions small amounts of cadmium invariably remained undeposited, but these were readily collected and determined by evaporation and weighing as sulfate.

Furthermore, our cell was so constructed of glass that it contained the anode as well as the cathode, so that any attacking of the anode by the free chlorine merely resulted in the transfer of platinum from one part of the weighed apparatus to another; and the cell was so nearly closed that explosions of liquid during the drying of the amalgams could cause no loss of mercury.

Contrary to the experience of Quinn and Hulett, we observed no blackening of mercury or electrolyte during electrolysis. This, however, may have been caused by the platinum beaker used by them as cathode.

Purification of Cadmium Chloride.

Although it seemed unlikely that salts of foreign metals in the cadmium material were the cause of the difficulty, yet a large portion of our

¹ THIS JOURNAL, 33, 888 (1911).

energy was spent in the purification of the cadmium. Furthermore, the purity of the different preparations was very carefully followed by photographing the spark spectrum with metallic electrodes in a Féry quartz spectrograph which covered the range 2100–6000 μ . The most difficult impurity to eliminate from cadmium is lead, but we were able to show that no one of our preparations contained a quantity of lead large enough to affect the observed atomic weight of cadmium, and some of the material was wholly free from lead, so far as we could determine.

The spectrographic method of detecting impurities is, of course, a sensitive one. In most cases, extremely small proportions of impurities appear unmistakably in the photograph. For instance, lead analyzed by Mr. F. L. Grover in this laboratory, and found to contain less than 0.004% of copper gave a spectrum in which the two strong copper lines were very prominent, while in the spectrum of one of our samples of crude cadmium, containing 0.2% of lead, the lead line of wave length 4058 was as prominent as many of the strong cadmium lines. None of our material could possibly have contained as much as one-tenth of this quantity, yet 0.02% of lead would raise the apparent atomic weight of cadmium by only 0.01 unit. The difficulty in analyzing material containing only spectroscopic traces of impurities has prevented our finding the limit of sensitiveness of the method in the case of cadmium and lead, but this subject in general is under investigation in this laboratory. We have assumed the complete or almost complete disappearance of the lines of impurities in the spectrum to be an indication that sufficient purity has been attained.

The first specimen of cadmium with which we started was found, spectrographically, to contain about 0.1% lead, a trace of copper, considerable nickel, and traces of thallium, indium and calcium. No zinc lines could be seen in the spectrogram, and subsequent analysis in the wet way confirmed the surprising conclusion that zinc was not present. The purification of this material by electrolysis with a dissolving anode was first attempted. Various electrolytes were tried, the most satisfactory from the standpoint of a compact cadmium deposit being a slightly acid solution of the chloride. If the solution was neutral, basic salts were precipitated. During the electrolysis thallous chloride was gradually deposited on the bottom of the dish. The small crystals of metal which separated were frequently raked toward the platinum cathode by means of a glass rake in order to prevent short-circuiting, but occasionally were removed, and after thorough washing with water centrifugally drained. The crystals were then fused in a thoroughly leached "alundum" boat in a current of electrolytic hydrogen. Electrodes made from this metal gave a spectrum in which only lead and copper lines could be seen in addition to the cadmium spectrum, the lead lines of essentially the original intensity, the copper lines considerably reduced in intensity. Since

a second electrolysis with an electrolyte made from the pure metal produced very little further diminution in the proportions of impurity, the electrolytic method of purification was then discontinued. The crystalline metal from the second electrolysis was washed, dried and fused as before.

Next, the buttons of metal were cleaned by etching with dilute hydrochloric acid and then were dissolved in hydrochloric acid containing a small amount of nitric acid in a quartz flask. Both acids were distilled through quartz condensers previous to use. As soon as the cadmium had dissolved, the solution was evaporated to small bulk four times with a large excess of hydrochloric acid, in order to remove nitric acid, and the salt was twice crystallized from the solution saturated with hydrochloric acid gas, as the acid chloride. The crystals were dried in a vacuum desiccator over caustic soda. This salt was found to contain a small proportion of ammonium chloride, formed presumably by the action of the metal on the nitric acid during solution, but since this ammonium chloride was volatilized during the subsequent fusion of the cadmium chloride, it could do no harm. This specimen of chloride is Sample A.

Since Sample A, after fusion in a current of hydrochloric acid, was found to contain a small amount of black residue, apparently carbon and silica, as will be shown later, the attempt was made to eliminate the difficulty by fusing the salt in a current of hydrochloric acid before crystallization. The mother liquors of Sample A, containing much hydrochloric acid, were used to dissolve more of the twice electrolyzed cadmium, with the help of a small amount of nitric acid, all in a quartz flask. The solution was evaporated to small bulk several times with a large excess of redistilled hydrochloric acid to eliminate the nitric acid. Nearly all the excess of hydrochloric acid was expelled by evaporation in quartz, and then evaporation to dryness in a platinum vessel followed. The dry salt was then fused in platinum boats in a current of hydrochloric acid gas, purified and dried by an apparatus described later, in a quartz tube. When the fused salt was dissolved, a considerable quantity of the black residue was found. This was removed by filtration on a platinum-sponge (Gooch-Munroe-Neubauer) crucible, in such a way that the solution came in contact only with platinum and quartz. The crystals obtained by evaporating the solution in a platinum dish and cooling were crystallized from solution in pure water a second time. This salt is designated Sample B. The yield was small because of the small temperature coefficient of solubility of the chloride.

From the mother liquors of the second crystallization metallic cadmium was obtained by electrolysis between platinum electrodes. Spark electrodes made from this metal by drawing the melted material into hard glass capillaries showed very faintly the lead line 4058, and the copper lines 3247 and 3273, but we estimate the proportions of these impurities

to be certainly less than 0.005%. No platinum lines could be seen.

Sample C was purified first by fractional precipitation of the sulfide with scrubbed hydrogen sulfide gas, as previously done by Baxter and Hines. From a dilute solution of cadmium chloride two small fractions were precipitated and rejected, then nearly all the remainder of the cadmium was precipitated in three fractions. These fractions were thoroughly washed with water, then dissolved in hydrochloric acid and reprecipitated. The first two fractions were combined and dissolved in redistilled sulfuric acid containing enough nitric acid to produce solution, for the red modification of cadmium sulfide formed during the washing of the sulfide does not easily dissolve. The third fraction, the most soluble, was not investigated in this research, since it corresponds to Sample D. The solution of the first two fractions was evaporated in a platinum dish until fumes of sulfuric acid were given off, and allowed to cool. Nearly all the sulfate remained insoluble in the excess of acid. After centrifugal drainage the salt was recrystallized by solution in water and precipitation by the addition of redistilled sulfuric acid, a far more economical and rapid process than crystallization from water. From a water solution of the product, metallic cadmium was deposited electrolytically upon a platinum dish as a loosely coherent mass of crystals, which were leached with water as thoroughly as possible. The greater part of the deposit was dissolved in distilled hydrochloric acid in the platinum dish, and the solution was evaporated to dryness in a quartz dish. In order to precipitate any platinum which might have been dissolved during the solution of the cadmium, a neutral solution of the residue was warmed with a portion of the original electrolytic metal in a platinum dish for some time. After filtration through a Gooch-Munroe-Neubauer crucible, the solution was again evaporated to dryness in a platinum dish and the residue was fused in a current of hydrochloric acid gas, as subsequently described. The fused material was dissolved in water, filtered through platinum sponge, and twice crystallized in platinum. The mother liquor from the first crystallization was tested for sulfate with negative results, showing that if the electrolytic deposit occluded any of the sulfate electrolyte, this must have been removed during the fusion of the chloride in hydrochloric acid. This fusion also served to char any residual organic material and also to separate the greater part of the silicic acid. Metal made from the mother liquors of the final crystals, when examined spectroscopically, showed faint traces of lead, platinum, and copper.

Sample D consisted of material prepared in the earlier researches by Baxter and Hines. Cadmium sulfate which had been made from Sample III (the most soluble) of the sulfide fractionation in the earlier research, was electrolyzed, and the metal converted to chloride exactly as in the case of Sample C. Metal made from the mother liquor of the final cadmium

chloride crystals, when tested spectroscopically, was found to contain the merest traces of copper and platinum. This evidence was very satisfactory in showing that the material used by Baxter, Hines and Frevert was pure.

Samples E and F were purified by crystallization of cadmium bromide. This salt has a much larger temperature coefficient of solubility than either chloride or sulfate, and was found to give a far more rapid and convenient method of purification than any other which we tested. Several hundred grams of crude cadmium containing about 0.2% of lead and traces of copper and thallium, were covered with dilute hydrobromic acid solution and then dissolved by the addition of commercially pure bromine.

A slight excess of bromine was removed by boiling, and the solution was then heated with metallic cadmium for some time to precipitate the more strongly electropositive metals. The solution was evaporated, and the salt content subjected to fractional crystallization according to the diagram shown here. After the first three series of crystallizations the fractions were filtered through platinum sponge, and platinum vessels only were subsequently employed. Metal prepared from the crystals

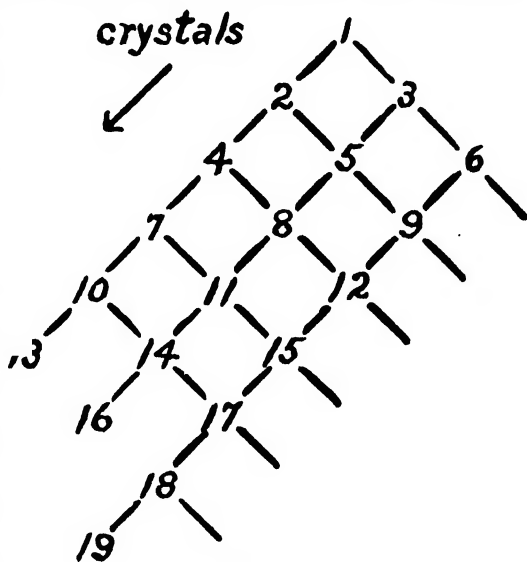


Fig. 1.

of Fraction 11, so far as could be found out from spectrograms, was free from impurity of any kind.

To prepare Sample E, Fraction 13 was converted to chloride by heating in a current of chlorine, as subsequently described. To prepare Sample F, Fractions 16 and 19 were combined, dissolved in hot water in a quartz flask, and a current of pure chlorine was passed in until all bromine had been expelled. The solution was then evaporated, the salt fused, dissolved, filtered and crystallized as with the other samples. Owing to an accident this material was lost after one analysis had been made.

In the crystallization of the cadmium chloride, owing to the high solubility of the salt, a large proportion of each sample remained in solution in the mother liquors. These were preserved in either quartz or platinum. To prepare Sample G these were combined, evaporated to crystallization,

and the crystal product twice recrystallized. Owing to increased experience in crystallizing cadmium chloride, and to the large amount of available material, these crystallizations were more satisfactory than the earlier ones. This was shown by the fact that metal prepared from the mother liquor of the last crystallization was spectroscopically pure.

Purification of Other Materials.

Water.—All the water was purified by double distillation, first from alkaline permanganate, then from very dilute sulfuric acid. Block-tin condensers were employed, no rubber or cork being used to connect the retort to the condenser. Frequently the water was received in platinum or quartz vessels, otherwise Jena flasks or non-sol bottles were used for storage.

Sulfuric Acid.—This substance was distilled from a non-tubulated glass retort into an air-cooled Jena glass receiver, with rejection of the extreme portions.

Alcohol.—Alcohol was distilled in glass, twice from lime and once from mercury. Fifty cubic centimeters upon evaporation in a quartz crucible left a residue which weighed 0.00016 g. before, 0.00006 g. after gentle ignition. In another experiment 200 cc. of water, 50 cc. of alcohol and 5 cc. of distilled hydrochloric acid were evaporated in a quartz dish, transferred to a platinum crucible and ignited gently with a drop of sulfuric acid. The crucible gained 0.00001 g.

Mercury.—Relatively pure mercury was three times distilled in vacuum.

Preparation of the Cadmium Chloride for Analysis.

The cadmium chloride was dried in preparation for weighing by fusion in a stream of dry hydrochloric acid gas. During this treatment the salt was contained, in the first three analyses, in a platinum boat, but usually in a quartz boat. The boat was placed in a quartz tube, which formed part of a "bottling apparatus,"¹ by means of which the boat could be transferred to the weighing bottle in which it was originally weighed without being exposed to moist air even for an instant.

The hydrochloric acid was generated by the action of the purest commercial concentrated sulfuric acid upon either fuming hydrochloric acid or sodium chloride, and the gas was dried by passing through five towers about 30 cm. long and 4 cm. in diameter, filled with glass beads moistened with concentrated sulfuric acid. Nitrogen was prepared by the Wanklyn method of passing air through concentrated ammonia solution and then over hot copper. The excess of ammonia was removed in two Allihn gas washing bottles containing dilute sulfuric acid, and the nitrogen was purified and dried by passing through towers containing silver nitrate solution, solid potassium hydroxide, concentrated sulfuric acid.

¹ Richards and Parker, *Proc. Amer. Acad.*, 32, 59 (1896); *Z. anorg. Chem.*, 13, 85.

and resublimed phosphorus pentoxide. Air was purified by reagents similar to those used in the purification of the nitrogen. The apparatus for generating and drying the hydrochloric acid was constructed wholly of glass, and the nitrogen and air purifying trains had rubber connections only at the beginning. Preliminary to fusion, the salt was heated gently by means of either an aluminum block furnace or an electric heating coil of "Nichrome" wire until the greater portion of the water had been expelled by efflorescence. The temperature then was raised until the salt was fused, and was maintained at this point for about fifteen minutes in order to insure the expulsion of a possible impurity of either ammonium salt or acids other than hydrochloric. After the salt had been allowed to cool, the hydrochloric acid gas was displaced first by a current of pure dry nitrogen, then by dry air. The boat was next transferred to the weighing bottle inside the "bottling apparatus," the weighing bottle was placed in a desiccator, and, after the desiccator had stood near the balance for at least an hour, the bottle and boat were weighed.

When salt treated as above is dissolved in water, a small amount of black material is left insoluble. Evidence was obtained in the course of this and other work which indicates that this material is largely carbon, but that it may contain silica. The source of the organic matter from which the carbon is produced by charring is not certain. Atmospheric dust and lint are undoubtedly responsible for a portion, the reagents and filters for the remainder. Preparing the hydrochloric acid gas from fused sodium chloride and concentrated sulfuric acid which had been heated with a small amount of permanganate until colorless, produced little or no diminution in the extent of the difficulty, which eliminates the gas in which the salt was fused as the cause. The source of the silica was probably the quartz dishes in which the concentrated solutions were heated.

The proportion of black material can be very much reduced by fusing the salt in hydrochloric acid, dissolving and filtering through a platinum sponge crucible preparatory to crystallization. This was done with all the preparations, except Samples A and E. A very considerable amount of black residue, obtained in purification of one of the samples, gave the evidence concerning the nature of the substance. This was filtered upon a Gooch-Munroe-Neubauer crucible, washed and dried. Upon gentle ignition, the carbon obviously burned, leaving a gray residue which was insoluble in a microcosmic salt bead. Mr. F. L. Grover in an investigation upon lead halides obtained similar evidence.

As has been stated, by suitable purification the proportion of black residue was made very low. In one experiment this was filtered upon a weighed Gooch-Munroe-Neubauer crucible and was found to weigh only 0.00002 g. Mr. Grover has found in lead chloride and bromide, similarly contaminated, in thirty-six experiments on an average 0.004% of black

residue, but the lead salts were not fused prior to crystallization and were to be expected to contain, and apparently did contain, more of the impurity than any cadmium chloride sample, except Sample A which was not fused before crystallization. Evidently, the error produced by the residue at the most could not be large. But in the analysis the difficulty partially took care of itself, for a portion of the residue adhered to the amalgam and was weighed with it, while a portion was evaporated with the washings and upon ignition was burned. Under the circumstances no attempt has been made to correct for whatever slight error may have been introduced.

With Samples E and G, the residue was almost, if not quite, eliminated. Sample E was made from cadmium bromide by heating and eventually fusing in a current of pure dry chlorine containing a small amount of hydrochloric acid gas, the conversion being conducted in the quartz boat in which the salt was finally weighed. The salt was then fused in pure hydrochloric acid gas as described above. Some difficulty was experienced by persistent retention of chlorine gas by the salt even when re-fused in pure hydrochloric acid gas, and, therefore, fusion in the latter atmosphere was prolonged considerably to ensure complete elimination of the chlorine.

Sample G of cadmium chloride also was fused for some time in chlorine before fusion in hydrochloric acid, and no residue could be seen in either the fused salt or its solution.

The chlorine gas in which the salt was fused was generated from manganese dioxide and concentrated hydrochloric acid, and was scrubbed with wet glass wool, charged with hydrochloric acid gas in four towers containing beads moistened with concentrated acid, and dried in four towers of beads wet with concentrated sulfuric acid. The apparatus was constructed wholly of glass.

In the first three analyses a platinum boat was used to contain the salt. In the first analysis it lost 0.00013 g., in the second, 0.00009 g. This is in accord with other experience in the Harvard Laboratory in the fusion of chlorides in platinum boats in a current of hydrochloric acid gas. It is seldom that the loss in weight of the boat is even as large as the above if the acid gas is free from air. On the other hand, if the hydrochloric acid contains air, the platinum may be very seriously attacked. Since this is not at all in accord with the experience of Quinn and Hulett, who report a loss as high as 2.9 mg. in one experiment, one cannot avoid the suspicion that their fusion atmosphere was not free from air. Because of convenience in manipulation rather than for any other reason, in the later analyses quartz boats were used. One of these in nine fusions lost 0.00013 g., while the weighing bottle, which was rinsed in each experiment, and the boat together lost 0.00033 g. Such constancy is all that could be desired. The average weight of the weighing bottle and boat before and after the fusion of the salt was used in the calculations.

The Electrolytic Cell.

In our earlier experiments upon the electrolytic method we attempted to deposit the cadmium and chlorine simultaneously, the former in a mercury cathode, the latter substance upon a silver anode. We met the same difficulty which other experimenters seem to have found in trying to deposit relatively large amounts of halogen in this way, in loosening of the silver halide deposit from the electrode, owing apparently to local complete conversion of the silver to halide.

The problem of disposing of the chlorine otherwise might have been solved as was done by Quinn and Hulett, by converting the chloride to sulfate before electrolysis. Such a step is entirely unnecessary, however, for a platinum electrode of moderate surface is imperceptibly attacked by the evolution of large amounts of chlorine upon it. For instance,

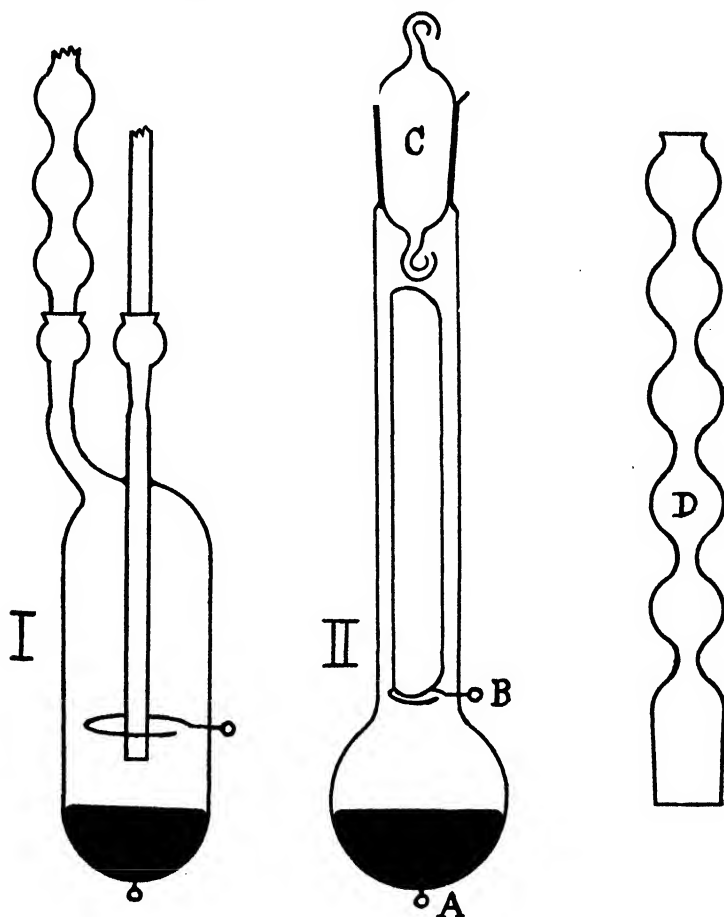


Fig. 2.

Easley¹ in the electrolysis of 125 g. of mercuric chloride found a platinum wire which served as anode to have lost in weight only 0.00015 g. One experiment of our own confirmed this constancy, for a weighed platinum wire anode lost no weight whatever in the electrolysis of several grams of cadmium chloride. Nevertheless, in order to make sure that no difficulty should be met from this source, a cell was constructed of glass with both cathode and anode permanently sealed in place. Thus any metal dissolved by chlorine liberated at the anode would almost immediately be deposited upon the cathode.

In the cell of Form I, in which the first two analyses were carried out, the salt after fusion was dissolved, and the solution was quantitatively transferred to the cell. The closed form was chosen at first in order to facilitate washing the amalgam and to prevent loss of mercury or amalgam by spurting while being dried at reduced pressure. In the later analyses the Form II was employed. The tube of this cell was large enough so that the boat, usually quartz, could be introduced bodily. During electrolysis it was supported upon the anode B, and at the end of the electrolysis it was removed before the amalgam was washed and dried.

The column of bulbs, D, ground into the neck served to catch spray formed during electrolysis. The stopper C was used to prevent loss of mercury by spurting during drying under low pressure, and always was weighed with the cell.

This cell was found particularly satisfactory in every way, and will be used for the exact analysis of other metallic halides in this laboratory.

Method of Analysis.

The cell was carefully washed and provided with a charge of thrice redistilled mercury, which had previously served as cathode during the electrolysis of dilute sulfuric acid for many hours, and was then several times rinsed, at first with water, then with alcohol. The outside also was cleaned with water and alcohol and wiped with a clean lintless cloth. In order to dry the cell and contents it was placed in a tubular desiccator containing fused potassium hydroxide and the pressure was reduced by a mechanical pump to a few millimeters. When the alcohol had evaporated, the cell was transferred to a second vacuum desiccator, containing fresh potassium hydroxide, for two hours. Finally it was placed with its counterpoise in still a third exhausted desiccator with solid potash where it was allowed to stand several hours before being weighed.

When the Cell I was used, the salt contained in the boat was dissolved in the minimum amount of water and the solution was introduced through the central tube. The boat was rinsed and the more concentrated rinsings added to the solution. The more dilute rinsings of the boat, as well as of

¹ THIS JOURNAL, 32, 1123 (1910).

the weighing bottle which originally contained the boat, were evaporated to small bulk in quartz or platinum and added to the main solution. During the electrolysis a slow current of the purest hydrogen was bubbled through the central tube.

When Cell II was used, the quartz boat containing the fused salt was transferred from the weighing bottle to the cell, and the salt was dissolved in the rinsings of the weighing bottle. The column of bulbs was inserted and last of all a small trap at the top of the column of bulbs.

The electrolysis was then started, at first with a current strength of a few tenths of an ampere. Later, when the greater portion of the cadmium was deposited, the current was increased until for the last two hours a potential of about 16 volts was maintained between the electrodes, the current strength being about one ampere. In all, about seven hours were consumed in each experiment. Gases evolved, at the anode at first, later at both electrodes, stirred the solution sufficiently well without other assistance. Toward the end of the electrolysis the column of bulbs was several times rinsed into the cell. In order to prevent heating of the cell, it was kept immersed nearly to the neck in clean, cold water during all of the electrolysis, and during the latter part, when the voltage was high, ice water was used.

At the end of the electrolysis, although practically all the metal was deposited and little chlorine was evolved upon the anode, yet a very considerable residual conductivity persisted with the evolution of hydrogen and oxygen. This was puzzling at first, but the cause was soon found to be the formation of a small amount of perchloric acid during the electrolysis.

When the deposition of the cadmium was essentially complete, *i. e.*, at the end of about seven hours, the cell was rinsed thoroughly with the purest water which had been saturated with the purest electrolytic hydrogen. The rinsing was accomplished by siphoning the liquid from the bottom of the cell into a clean flask and adding water at the top. Needless to say, the voltage between the electrodes was kept at a maximum during this preliminary washing. As soon as the cell was apparently clean, as indicated by a zero reading on the ammeter, it was disconnected from the battery circuit and further rinsed with water, the amalgam being agitated gently to dislodge any liquid which might have been imprisoned between the amalgam and the glass. Then the cell was rinsed with three 5 cc. portions of alcohol. The stopper was now inserted, the outside of the cell was cleansed with water and alcohol and dried with a clean cloth and the cell was placed in a vacuum desiccator. The drying of the amalgam was effected exactly as in the case of the mercury. In almost every experiment the amalgam was bright in appearance.

The aqueous and alcoholic rinsings were combined and evaporated in

a quartz dish over an electric stove. When in small bulk they were transferred to a weighed platinum crucible and after the addition of a drop of redistilled sulfuric acid, they were evaporated to dryness. The residue was ignited to very dull redness and weighed. By precipitation with hydrogen sulfide and colorimetric comparison with standards, this residue was shown to consist chiefly of cadmium sulfate, but it may have contained traces of alkalis and silica extracted from the glass cell. Since, however, the weight of the residue was seldom as much as a milligram, and frequently much less, the assumption that the residue was cadmium sulfate in applying a correction could not have introduced any considerable error. In fact, the agreement of the experiments where the residue was unusually large with those where the residue was small emphasizes the legitimacy of such a correction.

The fact that we were never able to secure complete deposition of the cadmium is interesting in connection with the statement by Quinn and Hulett that no cadmium could be detected in the residual electrolyte of their experiments. They tested for cadmium by means of hydrogen sulfide and say "we evaporated all our electrolytes to one cubic centimeter and tested each in this manner, so there was little chance for any cadmium to escape deposition without being detected." With a four-gram sample of cadmium chloride such as they used, this "one cubic centimeter" would consist mainly of pure sulfuric acid. It is obvious that, unless this sulfuric acid were previously expelled, even large amounts of cadmium might have escaped detection in the residual electrolyte. In order to find out whether complete deposition of the cadmium really can be secured, Mr. M. R. Grose, with a cell like those used in our analyses, electrolyzed about four grams of once recrystallized cadmium sulfate, the current strength at the end being about one ampere, as in Quinn and Hulett's experiments. The electrolyte was carefully removed and evaporated, finally at a temperature sufficiently high to vaporize the sulfuric acid. The residue weighed only 0.7 mg., and while it contained cadmium, was obviously not wholly cadmium sulfate. The experiment was repeated with salt very carefully prepared from the pure bromide and the residue, which in this experiment weighed 0.5 mg., was found to contain about 0.2 mg. of cadmium sulfate. While it is thus unlikely that the error from incomplete deposition of the cadmium was large enough to explain the discrepancy in question, yet it is unfortunate that Quinn and Hulett did not evaporate their electrolytes to dryness in order to make certain that they contained neither cadmium nor any other substance. This is especially so since their cadmium chloride, which was prepared merely by dissolving purified metal, which had been distilled in hard glass, in hydrochloric acid in a Jena flask and evaporating to dryness in a platinum dish, was not subsequently crystallized. It must be said, how-

ever, that Quinn and Hulett, starting with weighed amounts of cadmium, were able to recover essentially all the metal by an electrolytic process similar to the analytical procedure.

In order to find out whether the cadmium amalgam, upon exposure to air, oxidizes continuously, about 75 g. of amalgam were placed in an open platinum crucible and allowed to stand upon the balance pan with occasional weighing. The results were as follows:

| | |
|---------------------------------------|--------------|
| Weight after $\frac{1}{2}$ hr. | 104.09162 g. |
| Weight after $1\frac{1}{2}$ hrs. | 104.09158 g. |
| Weight after $2\frac{1}{2}$ hrs. | 104.09160 g. |
| Weight after agitation. | 104.09159 g. |

Although the amalgam seemed to be constant in weight, the possibility still existed that a superficial film of oxide formed at the outset might have an appreciable weight. This point was investigated in the following manner:

Several grams of pure cadmium were fused on an alundum boat in a current of the purest hydrogen. The resulting button was perfectly bright and clean. After standing in a desiccator for some hours it was weighed. The counterpoise of one of the cells was provided with about 80 g. of mercury and weighed by substitution for a similar vessel. The button was then introduced and after the cadmium had been allowed to amalgamate with the mercury, the system was weighed. The amalgam was of the same lustrous appearance as those obtained in the analyses.

| | Grams. |
|---|----------|
| Weight of vessel + mercury = counterpoise. | +1.69317 |
| Weight of cadmium. | 3.25227 |
| Sum. | 4.94544 |
| Weight of system after 7 hrs. = counterpoise. | +4.94555 |
| Weight of system after 31 hrs. = counterpoise. | +4.94547 |

If oxidation of the cadmium really occurs, the change in weight is evidently so slight as to be beyond the limit of error of weighing. The lustrous appearance of the amalgams obtained in the electrolyses is further evidence that little oxidation took place.

One experiment was carried out to test the constancy in the weight of the mercury during the washing and drying operations. The cell was prepared for weighing as usual, and weighed. Then it was washed with water and alcohol, dried in vacuum and reweighed. A loss in weight of 0.00007 g. was found.

Further evidence upon this point was obtained by electrolyzing a dilute hydrochloric acid solution in the cell, and after the customary rinsing and drying, determining the change in weight. Furthermore, the rinsings of the cell were evaporated with sulfuric acid in a weighed platinum crucible which was then reweighed. The results follow: The numbers in the col-

umn headed "possible error" are obtained as the algebraic sum of the "change in weight of cell" and "weight of residue" multiplied by 0.54, the proportion of cadmium in cadmium sulfate.

| Change in weight of cell. Gram. | Weight of residue. Gram. | Possible error. Gram. |
|------------------------------------|-----------------------------|--------------------------|
| -0.00001 | 0.00017 | +0.00008 |
| -0.00013 | 0.00012 | -0.00007 |
| -0.00004 | 0.00017 | +0.00005 |

Some of the residue may have been extracted from the column of bulbs used to catch the spray formed in the electrolysis which was not originally weighed with the cell. At all events, since the weight of the residue is divided by two before being applied as a correction, the uncertainty is obviously less than a tenth of a milligram.

For several reasons, error from evaporation of mercury is not to be feared. In the first place, at 20° the vapor pressure of mercury is 0.0013 mm., and the weight of a liter, therefore, 0.000014 g. The desiccators used for the preliminary exhaustion had volumes somewhat less than a liter, the one used for the final exhaustion a volume of about two liters. But since the pressure was not reduced much below a millimeter, practically only the interior of the cells became saturated with mercury vapor. Furthermore, evaporation from the amalgams would be less than from pure mercury. Finally, since the counterpoise was exhausted with the cell at the close, evaporation from it would at least partially compensate for evaporation from the cell. On account of the low vapor pressure of mercury at room temperature, however, the difficulty could not in any case have been serious. Since only about two liters of hydrogen were evolved at the cathode in each experiment, not more than 0.00003 g. could have been lost in this way even if the gas was saturated with mercury.

The weights were standardized to hundredths of a milligram by the substitution method described by Richards.¹ All weighings were made upon a No. 10 Troemner balance. With the heavier objects, such as the weighing bottle, and the cell containing mercury or amalgam, the balance beam was left down some minutes before making observations in order to allow the slight bending of the beam to occur. A small amount of crude radium bromide was kept in the balance case to prevent the objects weighed from retaining electrostatic charges. The weighing bottle and cell were always compared with counterpoises of very nearly the same shape, size and volume in order to avoid variations from changes in atmospheric conditions.

A vacuum correction of +0.000152 g. per gram of cadmium chloride was applied, the densities of the weights and the salt being assumed to be 8.3 and 4.047, respectively. The vacuum correction of cadmium dissolved in mercury was computed as follows:

¹ THIS JOURNAL, 22, 144 (1900).

| Temperature. | Density of mercury. | Concentration of amalgam. | Density of amalgam. | Vacuum correction per g. of dissolved cadmium. |
|--------------|---------------------|---------------------------|---------------------|--|
| 20° | 13.545 | 2.97 | 13.370 ¹ | —0.000017 |
| 25° | 13.534 | 3.00 | 13.354 ² | —0.000016 |
| 25° | 13.534 | 5.00 | 13.230 ² | —0.000015 |

An average vacuum correction of —0.000016 g. was, therefore, applied for every apparent gram of dissolved cadmium.

In a very few analyses the amalgam became so concentrated that a small amount of solid amalgam separated, but not in amount large enough to produce uncertainty in the vacuum correction.

Analyses 1 and 2 in the table of results were made with Cell I, and a platinum boat was employed. In Analysis 3 a cell similar to Cell II was used, but of considerably larger size. A platinum boat was used and introduced into the cell, where it was in contact with the anode during electrolysis, and was finally weighed with the cell. Allowance was then made for the weight of the boat at the outset. In all subsequent analyses a

THE ATOMIC WEIGHT OF CADMIUM.

Cd = 35.457.

| Number of analysis. | Sample of CdCl ₂ . | Weight of CdCl ₂ in vacuum. Grams. | Weight of Cd in vacuum. Grams. | Weight of CdSO ₄ residue. Gram. | Corrected weight of Cd in vacuum. Grams. | Ratio Cd : Cl. | Atomic weight of Cd. |
|--|-------------------------------|---|--------------------------------|--|--|----------------|----------------------|
| Preliminary Series. | | | | | | | |
| 1..... | A | 6.08570 | 3.73151 | 0.00055 | 3.73181 | 1.58538 | 112.426 |
| 2..... | A | 4.20489 | 2.57844 | 0.00036 | 2.57863 | 1.58562 | 112.443 |
| 3..... | A | 5.36203 | 3.28771 | 0.00085 | 3.28817 | 1.58553 | 112.436 |
| 4..... | B | 7.50512 | 4.60206 | 0.00028 | 4.60221 | 1.58538 | 112.426 |
| 5..... | B | 6.71591 | 4.11814 | 0.00046 | 4.11839 | 1.58551 | 112.435 |
| 6..... | B | 5.91556 | 3.62727 | 0.00067 | 3.62763 | 1.58555 | 112.438 |
| 7..... | C | 5.49323 | 3.36782 | 0.00042 | 3.36805 | 1.58483 | 112.387 |
| 8..... | B | 3.14416 | 1.92767 | 0.00044 | 1.92791 | 1.58513 | 112.408 |
| 9..... | C | 7.58705 | 4.65143 | 0.00056 | 4.65173 | 1.58474 | 112.381 |
| 10..... | B | 2.26738 | 1.38990 | 0.00030 | 1.39006 | 1.58444 | 112.359 |
| 11..... | B | 5.93501 | 3.63936 | 0.00048 | 3.63962 | 1.58562 | 112.443 |
| 12..... | F | 6.04122 | 3.70445 | 0.00084 | 3.70490 | 1.58578 | 112.454 |
| 13..... | D | 4.07400 | 2.49779 | 0.00077 | 2.49821 | 1.58537 | 112.425 |
| Final Series. | | | | | | | |
| 14..... | F | 9.00004 | 5.51844 | 0.00064 | 5.51879 | 1.58529 | 112.419 |
| 15..... | G | 6.56891 | 4.02776 | 0.00061 | 4.02808 | 1.58534 | 112.423 |
| 16..... | G | 7.12956 | 4.37074 | 0.00186 | 4.37174 | 1.58522 | 112.414 |
| 17..... | E | 8.57291 | 5.25636 | 0.00080 | 5.25679 | 1.58522 | 112.415 |
| 18..... | G | 7.76294 | 4.75854 | 0.00291 | 4.76011 | 1.58521 | 112.413 |
| Total..... | | 109.3659 | | | 67.0628 | 1.58530 | 112.420 |
| Average..... | | | | | | 1.58529 | 112.419 |
| Average, rejecting Analyses 10 and 12..... | | | | | | 1.58535 | 112.421 |
| Average of Analyses 14 to 18..... | | | | | | 1.58526 | 112.417 |

¹ Richards and Forbes, Carnegie Inst., Publication No. 56, 13 (1906).

² Hulett and De Lury, THIS JOURNAL, 30, 1810 (1908).

quartz boat and the final type of cell were employed. In two analyses by mistake the voltage was considerably reduced just previous to the washing, and it was suspected that both cadmium and mercury dissolved by the free chlorine were still contained in the electrolyte. This conjecture was borne out by unusually large residues when the electrolyte was evaporated. Since mercury salts would have been lost by vaporization during the heating of the residue, the final result would be too low. This was apparently the case, the two results being 112.38 and 112.39. Because of the uncertainty and because a third analysis with the same sample of material (Sample D) was subsequently made, the two analyses affected by the accident are not included in the table. In the first analysis in which cadmium chloride which had been fused in chlorine was used, the chlorine was not completely expelled from the salt, as was indicated by a residual brown color. This analysis also yielded a slightly lower result than the average 112.39, and is omitted from the table. All other analyses are included.

It makes little difference how the results are treated. The final verdict is that the atomic weight of cadmium is essentially 112.42 ($\text{Cl} = 35.457$; $\text{Ag} = 107.880$), an outcome in exact agreement with the earlier work of Baxter, Hines and Frevert.

While the difference between the extremes is nearly 0.1 unit in the atomic weight of cadmium, yet, if the highest result and the lowest result are disregarded the extreme difference is nearly halved. Furthermore, the last five results, obtained with unquestionably the best material and after ample experience had been gained with the method, differ among themselves by only 0.010 unit. All things considered, the average of these last five determinations, 112.417, seems to us to represent most nearly the real verdict of the research.

It is worth noting that the *lowest* result in the table, 112.359, obtained with the smallest amount of chloride used in any of the experiments, is identical with the *highest* result obtained by Quinn and Hulett, 112.36. Furthermore, even without the correction for residue in the electrolyte, the average atomic weight of cadmium from our experiments is 112.39.

The average ratio of cadmium to chlorine obtained in Analyses 14 to 18, 1.58526, corresponds to the percentage 61.319 of cadmium in cadmium chloride, while Baxter, Hines and Frevert found the percentage of chlorine in the salt to be 38.681. The sum of the two is 100.000. So close an agreement is partly fortuitous, for a discrepancy of 0.001% would be extremely difficult to detect by any analytical method yet devised.

Summary.

1. Crystallization of cadmium bromide is found to be a very efficient and rapid method of purifying cadmium material.

2. A modified form of electrolytic cell utilizing a mercury cathode for the direct electrolysis of chloride solutions is described.

3. The percentage of cadmium in anhydrous cadmium chloride is found to be 61.319, while Quinn and Hulett found only 61.298%. The former percentage corresponds to an atomic weight of cadmium of 112.417 ($Cl = 35.457$), a value which is in perfect agreement with the earlier one found by Baxter, Hines and Frevert, 112.418. If chlorine is taken at 35.458, the atomic weight of cadmium becomes 112.421.

The analysis of cadmium bromide by a similar method is now under way in this laboratory, and the results closely confirm the higher value for the atomic weight of cadmium. The method will also be applied to the analysis of other metallic halides.

We are greatly indebted to both the Carnegie Institution of Washington and the Elizabeth Thompson Science Fund for very generous assistance which has enabled us to obtain apparatus best suited for the work.

CAMBRIDGE, MASS.

THE ELECTROLYSIS OF SOLUTIONS OF THE RARE EARTHS.

BY L. M. DRNNIS AND B. J. LEMON.

Received November 18, 1914.

Historical.

But little attention appears to have been paid to the possibility of separating the rare earths by electrolysis of aqueous solutions of their salts. Edgar F. Smith¹ stated that "didymium is not precipitated, either as nitrate or acetate, although a partial precipitation takes place at the positive pole." Brauner² electrolyzed a solution of didymium acetate using platinum electrodes. There formed on the negative pole a pale red crystalline crust which contained didymium and acetic acid. Solutions of the nitrate and of the sulfate of didymium gave similar products. Brauner's object in these experiments was to ascertain whether a superoxide would appear on the positive pole. No such formation was noted, and he did not pursue the subject further. In a brief article entitled "Electrolysis of Solutions of the Rare Earths,"³ Krüss makes the following statement: "A solution of a chloride of a rare earth behaves upon electrolysis like a solution of an hydroxide in dilute hydrochloric acid; chlorine and hydrogen are set free at the electrodes, the solution loses more and more hydrochloric acid, and as the amount of the solvent diminishes, the hydroxide of the earth is precipitated in increasing amount. In this manner the rare earths can be removed from chloride solutions of mixtures of the earths, the amounts thus precipitated depending upon the

¹ *Ber.*, 13, 751 (1880).

² *Monatsh.*, 3, 1 (1882).

³ *Z. anorg. Chem.*, 3, 60 (1893).

strength of the current and the duration of the electrolysis. It is to be expected that those bases which are the weakest toward hydrochloric acid will first be precipitated as hydroxides as soon as a part of the hydrochloric acid is decomposed by the electrolysis. 'The stronger bases will remain in solution as the more stable chlorides. In order to remove the hydrochloric acid uniformly from all parts of the solution of the chlorides of the rare earths, electrodes of large surface were employed.' Krüss electrolyzed the solution for ten minutes, and then removed the heavy, dense deposit of hydroxide by filtration. 'The solution was then again electrolyzed for ten minutes, and in this manner small fractions of less than one gram each were obtained. Two electrolyses of solutions of impure yttria were carried out, and determinations of the atomic weights of the earths in the several fractions showed that the method gave quite rapid separation of the different earths. Krüss states at the close of this brief article that electrolysis of solutions of the rare earths might prove suitable for the separation of these elements. It does not appear, however, that he followed the matter further.

Considerable work has been done upon the anodic oxidation of cerium through electrolysis of solutions of cerium salts with platinum electrodes, but inasmuch as this does not concern the direct separation of the earth from solution upon electrolysis, the researches upon this subject will not here be reviewed.

Experimental.

Material.—The material that was employed in the experiments described below consisted of the earths of both the didymium and yttrium groups from which cerium and thorium had been removed. The earths of the didymium group were extracted from the crude double sulfates of potassium and the didymium group, a large amount of this material having kindly been presented to the writers by Dr. H. S. Miner of the Welsbach Light Company. The lanthanum and praseodymium nitrates were prepared from quite pure samples of these two salts that we owe also to the kindness of Dr. Miner. The earths of the yttrium group were obtained from the crude rare earth oxalates from xenotime: the mixture that was used in the experiments showed strong absorption bands of erbium, and rather faint bands of europium, samarium, and holmium. The didymium bands were very faint.

Apparatus.—The first electrolysis was performed in a small crystallizing dish and stationary electrodes of sheet platinum were used. On electrolyzing a slightly acid solution of the nitrates of the didymium group, no precipitate appeared until the free nitric acid had been broken down by the current. As soon as this had been effected, however, a separation of the hydroxides of the earths appeared at the cathode, and the internal resistance of the cell rapidly increased. Upon interrupting the current

and examining the contents of the cell it was found that a portion of the hydroxides had separated in flocculent form resembling aluminum hydroxide, and also that that part of the cathode which was immersed in the solution was heavily covered with a dense, granular precipitate of the hydroxides. It was this coating of the cathode surface that interfered with the passage of the current and caused marked fluctuations in the voltage.

It was thus evident that no definite voltage could be maintained for any considerable length of time unless the cathode surface could be kept free from deposit of the hydroxides. To attain this end, a rotating cathode of copper in the form of a wheel 15 cm. in diameter and 2.5 cm. in thickness was next employed. This was mounted on a horizontal shaft of the same material and was set in such position that the wheel dipped into the solution of the nitrates of the earth to a depth of three centimeters. An anode of platinum was used. A copper scraper was fastened in such position that it rested against the edge of the cathode wheel, and it was hoped that by means of this arrangement the deposit of hydroxides upon the cathode might rapidly be removed, and the voltage in this manner be kept sufficiently constant to permit of fractional decomposition of the different nitrates in solution. The apparatus did not give satisfactory results, and after thorough trial it was abandoned, and a mercury cathode was employed. The mercury was placed in a glass cell about 12 cm. in diameter and 13 cm. high, the layer of mercury being about three centimeters deep. The surface of this mercury cathode was kept clean by violently agitating it by jets of air, the air being conducted into the mercury through a glass tube with three outlets. The anode consisted of a piece of platinum wire 0.76 mm. in diameter. The source of current was a set of eight storage cells, an ammeter and variable resistance were placed in series with the cell, and a voltmeter was connected in shunt with the cell. The aqueous solution of the rare earths that was to be subjected to electrolysis was placed in the cell upon the surface of the mercury.

I. Separation of Lanthanum from the Other Earths of the Didymium Group.

A neutral solution of the nitrates of the rare earths neodymium, praseodymium, lanthanum and samarium, that contained 50 g. of the oxides of the earths in one liter of the solution, was placed upon the mercury cathode in the cell, the mercury was set in agitation by a blast of air, the current was turned on, and the voltage was gradually stepped up to a point where fairly rapid precipitation of the hydroxides took place. The voltage was maintained constant at this value, 9 volts, throughout the series of fractionations, and this voltage was used in the three fractional electrolyses described below. The first fractional electrolysis was of six hours' duration. The current was then turned off, the hydroxides were

allowed to settle, the clear supernatant liquid was siphoned off, and the remaining solution was separated from the precipitate by filtration through a Büchner funnel. The filtrate was then returned to the cell and was again electrolyzed. In this manner eleven fractions were obtained. The hydroxides of each fraction were first thoroughly washed with hot water, were then dissolved in hydrochloric acid, and the small amount of mercury that they were found to contain was removed by double treatment with hydrogen sulfide. The rare earths in the solution were then precipitated from a slightly acid solution with oxalic acid, were thoroughly washed, and were then ignited to the oxides. The atomic weights of the rare earth elements were determined by igniting one portion of the oxalate to oxide and determining the oxalic acid in another portion by titration with potassium permanganate. The details of this run are shown in Table I.

TABLE I.—SEPARATION OF LANTHANUM FROM OTHER EARTHS OF THE DIDYMIUM GROUP.

| Number of fraction. | Time in hours. | Color of oxides. | Atomic weights (original material, 140.6). |
|------------------------|----------------|------------------|--|
| 1..... | 6 | Light brown | 140.9 |
| 2..... | 5 | Light brown | 141.2 |
| 3..... | 7 | Light brown | 141.5 |
| 4..... | 6 | Light brown | 141.9 |
| 5..... | 4 | Color fading | 141.7 |
| 6..... | 5 | Color fading | 141.0 |
| 7..... | 4 | Color fading | 140.4 |
| 8..... | 5 | Color faint | 139.6 |
| 9..... | 3 | Color very faint | 139.5 |
| 10..... | 4 | White | 139.0 |
| Residual solution..... | .. | White | 138.9 |

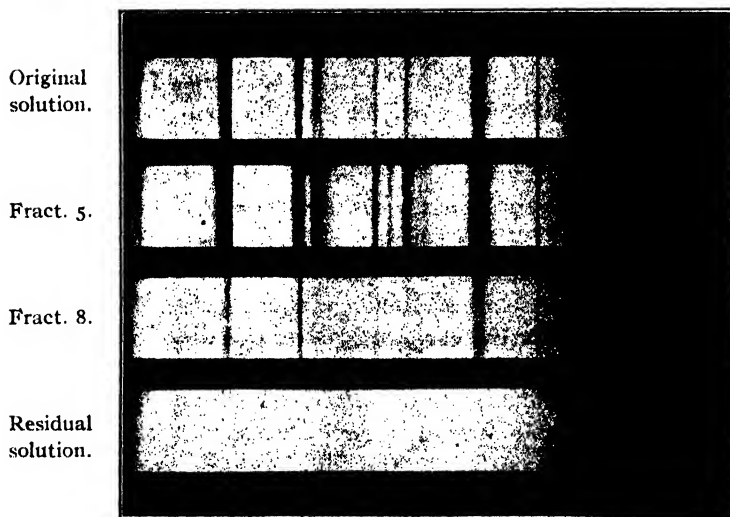


Plate I.

The absorption spectra of the original solution of Fractions 5 and 8, and of the residual solution were photographed with the aid of a Hilger wavelength spectrometer, Model 1912, with an oxyhydrogen zirconia lamp as the source of illumination. The different solutions used were of the same concentration in respect to the weight of the rare earth oxides contained in a unit volume. For photographs in black and white the Cramer trichromatic plate, which is especially sensitive to the red, was found to give quite satisfactory results (Plate I).

II. Separation of Lanthanum from Praseodymium.

Nineteen and six-tenths grams of fairly pure praseodymium dioxide and 18.9 g. of lanthanum oxide were mixed, dissolved in nitric acid, the solution twice evaporated to dryness, redissolved in water, and diluted to 500 cc. Upon electrolysis of this solution the results shown in Table II were obtained.

The atomic weights of the rare earth elements in these fractions were determined by the method mentioned under I. Inasmuch as praseodymium was present, the active oxygen in the ignited oxide was determined by the Bunsen method and this was deducted from the weight of the oxide

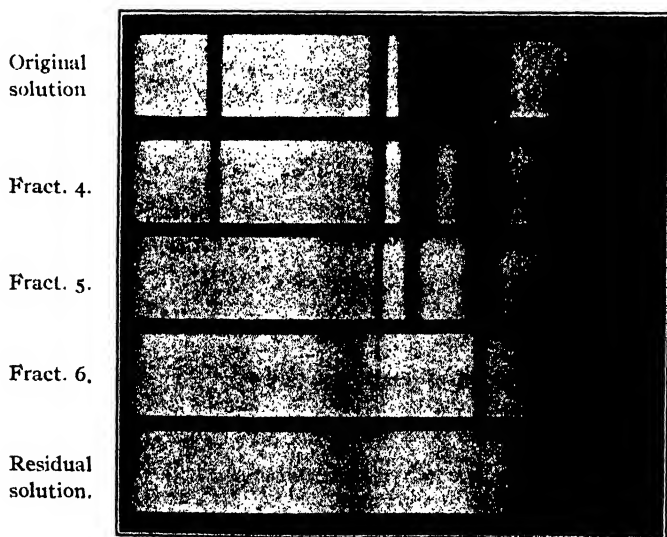


Plate II.

in order to arrive at the amount of Pr_2O_3 that was present. That the atomic weights of the earths in Fractions 1 to 4 inclusive were higher than that of praseodymium is due to the fact that small amounts of other earths of this group were present.

TABLE II.

| Number of fraction. | Time in hours. | Color of oxides. | Atomic weights, (original material 141.2). |
|------------------------|----------------|------------------------|--|
| 1..... | 9 | Black | 142.1 |
| 2..... | 7 | Black | 141.9 |
| 3..... | 8 | Dark brown | 142.0 |
| 4..... | 9 | Brown color fading | 141.7 |
| 5..... | 8 | Brown color faint | 140.3 |
| 6..... | 7 | Brown color very faint | 139.5 |
| Residual solution..... | .. | White | 138.8 |

Photographs of the original solution, of Fractions 4, 5 and 6, and of the residual solution are reproduced in Plate II. It will be noted that lanthanum is freed from praseodymium by a very small number of fractional electrolyses.

III. Fractional Electrolysis of the Earths from Xenotime. Separation of Erbium from Yttrium.

Six fractional electrolyses were made with the results as set forth in Table III.

TABLE III.

| Number of fraction. | Time in hours. | Color of oxides. | Atomic weights (original material, 103.85). |
|------------------------|----------------|-------------------|---|
| 1..... | 10 | Light yellow | 104.89 |
| 2..... | 8 | Light yellow | 111.00 |
| 3..... | 9 | Light yellow | 109.23 |
| 4..... | 7 | Light yellow | 99.73 |
| 5..... | 8 | Faint yellow | 93.50 |
| Residual solution..... | .. | Very faint yellow | 92.08 |

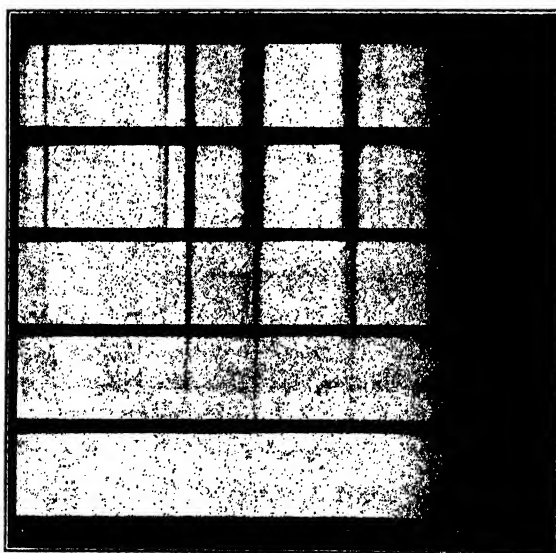
Original solution.

Fract. 3.

Fract. 4.

Fract. 5.

Residual solution.



* Plate III.

Photographs of the original solution, of Fractions 3, 4 and 5, and of the residual solution are reproduced in Plate III. It will be noted that erbium concentrated chiefly in the first three fractions and that in the succeeding fractions its amount rapidly decreased. The atomic weight of the rare earths in the final fraction, No. 6, was 92, which demonstrates the rapidity of the concentration of yttrium by this method.

The results of the experiments here described upon the fractional electrolysis of different mixtures of the rare earths appear to warrant the statement that the method yields quite rapid separations of some of the rare earths, and that these separations can be effected with far less expenditure of time and labor than by the customary methods of fractional crystallization or fractional precipitation.

CORNELL UNIVERSITY, ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

VACUUM AND PRESSURE STOPCOCKS.¹

BY MERLE RANDALL AND F. RUSSELL V. BICHOWSKY.

Received November 11, 1914.

The first essential of any stopcock of either hard or soft glass, no matter what its design, is that the glass be perfectly homogeneous and thoroughly annealed, as strains in either the key or frame will in time cause the stopcock either to jam or to leak. Unsymmetrical construction, whether due to poor design or poor workmanship, will, in general, have the same effect. Especially unfortunate is a lack of uniformity in the thickness of the walls of the frame.

Stopcocks of large taper in the key are easier to grind and polish than those of small taper, but are less satisfactory for the reasons that the key must necessarily be shorter, and that the lubricant has a greater tendency to float the key from the seat, especially when the stopcock is used under pressures slightly greater than that of the atmosphere. Careful grinding and very careful polishing are naturally essential.²

Probably the most serious defect of the ordinary straight-bore stopcock is the tendency of the bore to track bubbles and to scrape off the lubricant in its plane and thus allow leakage around the barrel.³ The diagonal-bore stopcock does not allow direct leakage in this way and is, in a measure, self-sealing. It should be pointed out that the key of diagonal-bore stopcocks should be longer than that of straight-bore stopcocks of the

¹ This paper is written in response to several requests for the specifications of the stopcocks in use in this laboratory.

² Morley, *Smithsonian Contributions* No. 980, p. 89 (1895).

³ This scraping and tracking can be partially prevented by proper construction of the apertures of the cross bore and frame.

same diameter, and that the slope of the bore should be sufficient to provide a wide ring of unscraped lubricant.¹

Diagonal-bore stopcocks, when used with the key in a vertical position in apparatus through which liquids are passed, are likely to trap some liquid in the bore of the stopcock. This is especially inconvenient when mercury is used, as in gas measuring apparatus. It can, however, be entirely prevented by the convenient arrangement of the tubes shown for a two way vacuum stopcock (Fig. 1). The principle is applicable to all other types.

TABLE I.—ORDINARY ONE WAY STOPCOCKS WITH SOLID KEY.²

| | Mm. | Mm. | Mm. | Mm. | Mm. | Mm. |
|--|-----|------|------|------|------|------|
| <i>Key:</i> | | | | | | |
| Bore of hole..... | 1.0 | 1.0 | 2.0 | 2.0 | 3.0 | 6.0 |
| Diameter, large end..... | 6.5 | 11.0 | 11.0 | 11.0 | 15.0 | 20.0 |
| Diameter, small end..... | 5.3 | 9.0 | 9.0 | 9.0 | 12.0 | 17.0 |
| Length of ground surface..... | 17 | 32 | 32 | 32 | 36 | 47 |
| Total length..... | 25 | 42 | 42 | 42 | 48 | 65 |
| <i>Frame and Tubing:</i> | | | | | | |
| Inside diameter of tubing..... | 1.0 | 1.0 | 2.0 | 3.0 | 6.0 | 12.0 |
| Thickness of walls of tubing..... | 1.0 | 2.0 | 2.0 | 1.5 | 1.5 | 1.5 |
| Length of tubing..... | 100 | 100 | 100 | 100 | 100 | 150 |
| Distance between tubing A and base of key..... | 6 | 12 | 12 | 12 | 13 | 15 |
| Distance between tubing A and B..... | 5.0 | 8.0 | 8.0 | 8.0 | 11.0 | 14.0 |

TABLE II.—ORDINARY TWO WAY STOPCOCKS WITH SOLID KEY.

| | Mm. | Mm. | Mm. | Mm. | Mm. | Mm. |
|---|------|------|------|------|------|------|
| <i>Key:</i> | | | | | | |
| Bore of hole..... | 1.0 | 1.0 | 2.0 | 2.0 | 3.0 | 6.0 |
| Diameter, large end..... | 6.5 | 12.0 | 12.0 | 12.0 | 15.0 | 21.0 |
| Diameter, small end..... | 5.0 | 9.0 | 9.0 | 9.0 | 12.0 | 17.0 |
| Length of ground surface..... | 22 | 44 | 44 | 44 | 47 | 60 |
| Total length..... | 36 | 60 | 60 | 60 | 65 | 80 |
| <i>Frame and Tubing:</i> | | | | | | |
| Inside diameter of tubing..... | 1.0 | 1.0 | 2.0 | 3.0 | 6.0 | 12.0 |
| Thickness of wall of tubing..... | 1.0 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Distance between centers of tubing A and C..... | 10.0 | 16.0 | 16.0 | 16.0 | 22.0 | 28.0 |
| Length of tubing..... | 100 | 100 | 100 | 100 | 100 | 150 |
| Distance between tubing A and base of key..... | 6 | 12 | 12 | 12 | 13 | 15 |

¹ Dr. C. A. Kraus of the Massachusetts Institute of Technology has used a large number of lubricants, and finds that, in general, the stiffer lubricants, such as the gutta percha lubricant recommended by Keyes (*Loc. cit.*), are the more satisfactory. With pressure stopcocks it is necessary to use a very much heavier lubricant than usual. Dr. Kraus has also pointed out a number of desirable features in regard to stopcocks for which we extend our thanks.

² The stopcocks described in Tables I and II are analogous to those shown in Figs. 2 and 3.

Specifications for various convenient sizes of ordinary diagonal-bore stopcocks are given in Tables I and II. Stopcocks made to specification are only slightly more expensive than the stock designs and we have found them much more satisfactory.

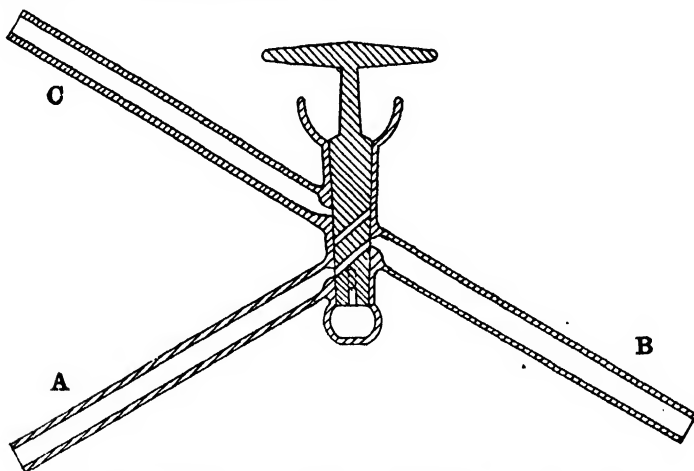


Fig. 1.—Self-draining two way vacuum stopcock. Keyes type.

Vacuum Stopcocks.—Of the various types of vacuum stopcocks only that described by Keyes¹ (Figs. 2 and 3) appears to be satisfactory.

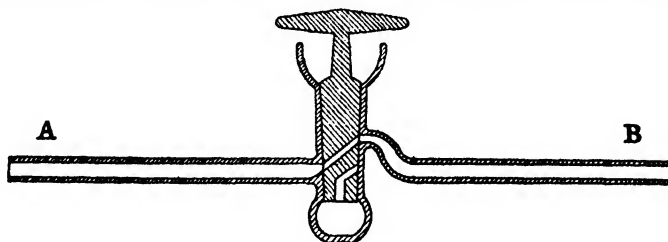


Fig. 2.—One way vacuum stopcock. Modified Keyes type.

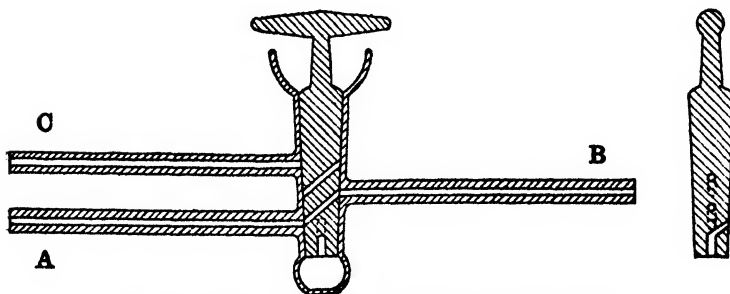


Fig. 3.—Two way vacuum stopcock. Keyes Type.

¹ Keyes, *Science*, 28, 735 (1902); *THIS JOURNAL*, 31, 1271 (1909).

In this type an extension of the small end of the frame is formed into a closed chamber which can be evacuated at will. Stopcocks having a similarly constructed chamber at the base, but having no means provided for evacuating it, are disadvantageous, as the air in the chamber is under a pressure slightly greater than that of the atmosphere and so tends to loosen the key and leak into the apparatus. Stopcocks of this type, however, can be readily converted into the Keyes type by boring suitable channels. Those stopcocks in which the small end of the barrel is formed into one of the connecting tubes are fairly satisfactory as long as this connecting tube is permanently connected with a vacuum, except that it has the disadvantages of the straight-bore type, is unsymmetrical, and is not as compact as the Keyes form. The cup that is left on the

TABLE III.—ONE WAY VACUUM STOPCOCKS WITH SOLID KEY; Cf. FIG. 2.

| | Mm. | Mm. | Mm. | Mm. | Mm. | Mm. | Mm. |
|---|-----|-----|-----|-----|------|------|------|
| <i>Key:</i> | | | | | | | |
| Bore of hole..... | 1.0 | 1.0 | 2.0 | 2.0 | 3.0 | 3.0 | 6.0 |
| Diameter, large end..... | 6.5 | 9.0 | 9.0 | 9.0 | 15.0 | 15.0 | 20.0 |
| Diameter, small end..... | 5.3 | 7.5 | 7.5 | 7.5 | 12.0 | 12.0 | 17.0 |
| Length of ground surface..... | 17 | 32 | 32 | 32 | 36 | 36 | 46 |
| Total length..... | 34 | 51 | 51 | 51 | 64 | 64 | 70 |
| <i>Frame and Tubing:</i> | | | | | | | |
| Inside diameter of tubing..... | 1.0 | 1.0 | 2.0 | 3.0 | 3.0 | 6.0 | 12.0 |
| Thickness of wall of tubing..... | 1.5 | 3.0 | 2.0 | 1.5 | 1.5 | 1.5 | 1.5 |
| Depth of vacuum seat..... | 6 | 10 | 10 | 10 | 10 | 10 | 10 |
| Length of tubing..... | 100 | 100 | 100 | 100 | 100 | 100 | 150 |
| Distance between tubing A and base of key..... | 4 | 8 | 8 | 8 | 10 | 10 | 12 |
| Distance between tubing A and B..... | 5.0 | 7.0 | 7.0 | 7.0 | 11 | 11 | 14 |

TABLE IV.—TWO WAY VACUUM STOPCOCKS WITH SOLID KEY; Cf. FIG. 3.

| | Mm. | Mm. | Mm. | Mm. | Mm. | Mm. | Mm. | Mm. |
|---|------|------|------|------|------|------|------|------|
| <i>Key:</i> | | | | | | | | |
| Bore of hole..... | 1.0 | 1.0 | 1.0 | 2.0 | 2.0 | 2.0 | 3.0 | 6.0 |
| Diameter, large end..... | 6.5 | 12.0 | 12.0 | 12.0 | 12.0 | 12.0 | 15.0 | 21.0 |
| Diameter, small end..... | 5.0 | 9.0 | 9.0 | 9.0 | 9.0 | 9.0 | 12.0 | 17.0 |
| Length of ground surface... | 22 | 44 | 44 | 44 | 44 | 44 | 47 | 60 |
| Total length..... | 40 | 70 | 70 | 70 | 70 | 70 | 75 | 90 |
| <i>Frame and Tubing:</i> | | | | | | | | |
| Inside diameter of tubing A and C..... | 1.0 | 1.0 | 2.0 | 2.0 | 3.0 | 3.0 | 6.0 | 12.0 |
| Inside diameter of tubing B | 1.0 | 1.0 | 2.0 | 2.0 | 2.0 | 3.0 | 6.0 | 12.0 |
| Thickness of wall of tubing.. | 1.5 | 2.0 | 2.0 | 2.0 | 2.0 | 1.5 | 1.5 | 1.5 |
| Distance between tubing A and C..... | 10.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 22.0 | 28.0 |
| Depth of vacuum seat..... | 6 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Length of tubing..... | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 150 |
| Distance between tubing A and base of key..... | 5 | 7 | 9 | 9 | 9 | 9 | 10 | 12 |

top of the Keyes stopcock is not intended to be filled with mercury, but is merely to catch the excess lubricant that squeezes out, or it may be filled with a very soft lubricant.¹

Specifications for various sizes of one and two way vacuum stopcocks are given in Tables III and IV.

Pressure Stopcocks.—No glass stopcock suitable for use under pressures has been described.² Professor G. N. Lewis and one of the writers have designed a pressure stopcock in which the taper of the key is reversed in direction and in which the base of the frame has been formed into a deep pressure seat (Fig. 4). This stopcock has been used in a number of investigations in this laboratory and has proven perfectly satisfactory when properly lubricated. The pressure is limited only by the breaking strength of the glass. The deep pressure seat and long handled stem are necessary in order that the stopcock can be properly lubricated.

The frame is first made with an extension M, (Fig. 4) which is afterwards sealed off at N as the last step in the process of assembly. The

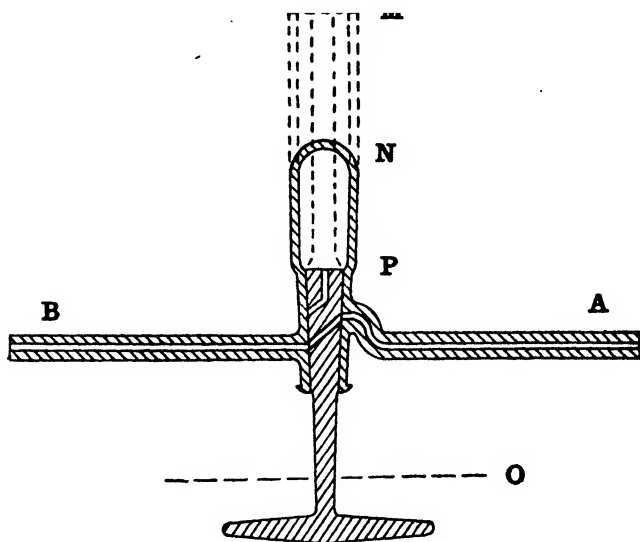


Fig. 4.—One way pressure stopcock. Lewis and Randall type.

¹ If it is desired, this cup may be filled with mercury, but it has been the experience of this laboratory that mercury does not increase the efficiency of a well ground and well lubricated stopcock, and is apt to float the key from the seat of one that is poorly made and lubricated.

² Since this paper was written, Professor W. A. Noyes has kindly called our attention to the fact that Dixon and Edgar (*Phil. Trans.*, (A) 205, 169 (1905)) have described a pressure stopcock in which the taper of the key is reversed. This stopcock, in which the pressure chamber is formed into one of the connecting tubes possesses the same disadvantages as the similar vacuum stopcock already discussed.

key of the stopcock is made without the handle below O, but with a long stem on the large end of the key as shown by the dotted lines. By means of this stem the key is then ground into the frame. The extension of the key is cut off at P and the holes are then bored into the key so as to register with the bore of tubes A and B. The handle is then sealed on below O and the base of the barrel sealed off at N. It is usually more convenient to use this stopcock in the inverted position shown in the figure. The stopcock may be made self-draining by inclining the tubes A and B. It has been found convenient to insert a coiled spring between the barrel and the handle in case the stopcock is to be used for vacuum as well as pressure. Satisfactory dimensions are given in Table V.

TABLE V.—ONE WAY PRESSURE STOPCOCK WITH SOLID KEY.

| | Mm. |
|--|-----|
| <i>Key:</i> | |
| Bore of holes..... | 1.0 |
| Diameter, large end..... | 9.0 |
| Diameter, small end..... | 7.0 |
| Length of ground surface..... | 30 |
| Total length..... | 70 |
| <i>Frame and Tubing:</i> | |
| Inside diameter tubing..... | 1.0 |
| Thickness of wall of tubing..... | 3.0 |
| Thickness of wall of frame..... | 3.0 |
| Depth of bulb, on pressure seat..... | 25 |
| Length of tubing..... | 100 |
| Distance between tubing A and base of key..... | 13 |
| Distance between tubing A and B..... | 7.0 |

Multiple Stopcocks.—The two way stopcock enables one to connect either of two parts of an apparatus separately to a third, but does not allow both to be connected at the same time with the third. Neither does it allow the first two parts to be connected. It is also sometimes desirable to connect more than three parts of an apparatus in various combinations. It is, of course, possible in most cases to accomplish this result by a more or less inconvenient arrangement of a number of one- and two way stopcocks. The straight-bore multiple stopcock is unsuitable for careful work, and cannot be used in apparatus under pressure or vacuum.

It is perfectly possible to combine the fundamental principles discussed in the previous sections and make multiple stopcocks of the diagonal-bore ordinary, vacuum or pressure type, as in Fig. 5, which shows a multiple way vacuum stopcock. The essential feature of this design is that the connecting tubes, which may be as many as are desired, are symmetrically placed about the barrel but upon different horizontal planes. The connection, E, to the vacuum seat is bored so that it registers with the lower of the connecting tubes, A, and is at such an angle that none of the other

holes register at the same time. Holes are then bored to a common center from the connecting tubes. The arrangement of these holes may

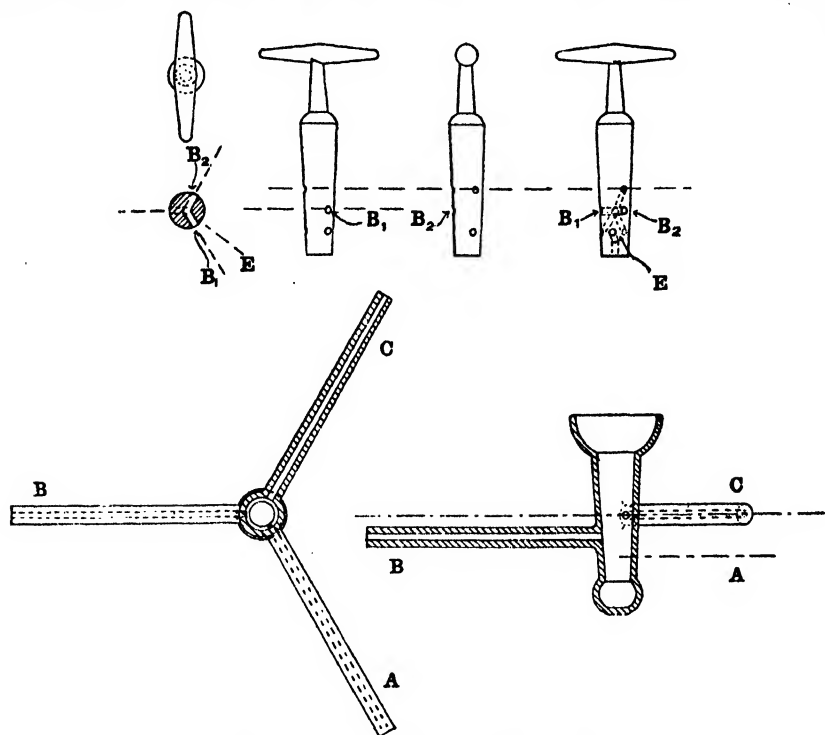


Fig. 5.—Multiple vacuum stopcock.

be varied to suit the particular purpose of the stopcock. In the stopcock shown, tube A, which is assumed to be connected to the pump may be

TABLE VI.—MULTIPLE VACUUM STOPCOCK WITH SOLID KEY.

| Key: | | Mm. |
|--------------------------------------|--|------|
| Bore of holes..... | | 1.0 |
| Diameter, large end..... | | 12.0 |
| Diameter, small end..... | | 9.0 |
| Length of ground surface..... | | 44 |
| Angle between A and B and C..... | | 120° |
| Angle between A and E..... | | 30° |
| Total length..... | | 70 |
| Frame and Tubing: | | |
| Inside diameter of tubing..... | | 2.0 |
| Thickness of wall..... | | 2.0 |
| Distance between planes A and B..... | | 6.0 |
| Distance between planes B and C..... | | 6.0 |
| Angle between A and B and C..... | | 120° |
| Depth of bulb..... | | 10 |
| Distance between A and base..... | | 8 |

separately connected with tube B or C, or B and C may be themselves connected. If, when tubes B and C are connected, a hole is drilled from A to the center, the stopcock will operate as a multiple way stopcock connecting either B or C, or both, to A. The dimensions of this stopcock are given in Table VI.

In conclusion, the authors wish to thank Professor G. N. Lewis and Mr. G. H. Fosdick for their kind suggestions.

BERKELEY, CALIF.

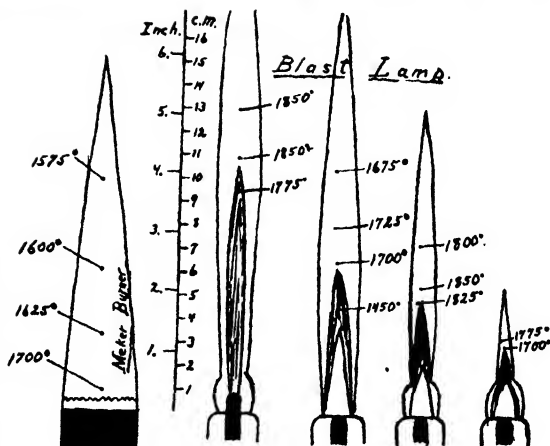
NOTES.

Blast-Lamp for Natural Gas.—The common blast-lamp may be rendered suitable for natural gas by connecting a T-tube to the gas inlet,

so that sufficient air may be introduced with the gas to give a blue flame before blowing air through the regular air nozzle. For thorough mixing of the gases a small mixing chamber is desirable. The illustration shows a lamp so modified, that has been in operation in this laboratory for almost a year, being used by students for



working glass as well as for heating crucibles. Flames of all sizes are secured almost as easily as with coal gas. Copper gauze was placed in the burner tube to prevent "flashing back," but later this precaution was abandoned, as our gas can not be made to "strike back" in any burner. A small thermocouple gave the flame temperatures indicated in the diagram.



JAMES C. McCULLOUGH.

A Modified Kipp Generator.—The diagram, Fig. 1, shows a gas generator which can be used to take the place of a Kipp. Especially adapted to individual student use in qualitative analysis, it ensures a ready supply of hydrogen sulfide gas at any moment.

Three gas bottles (ordinary gas collecting bottles will do just as well) are connected as shown. The reservoir bottle, *a*, which is free to move, contains a three hole stopper. A thistle-tube is inserted in one hole, a bent glass tube extending almost to the top of the bottle in the other hole, while through the third hole is inserted a short piece of glass tubing, *d*. A rubber tube (about 6 mm. bore) has one end attached at *d* and the other to the glass tube at *e* of the bottle *b*. Tube *f* extends almost to the bottom of the bottle *b*, and to the top of the stopper of bottle *c*. The other hole of the generating bottle *c* contains a piece of bent glass tubing closed by a pinch-cock, as shown.

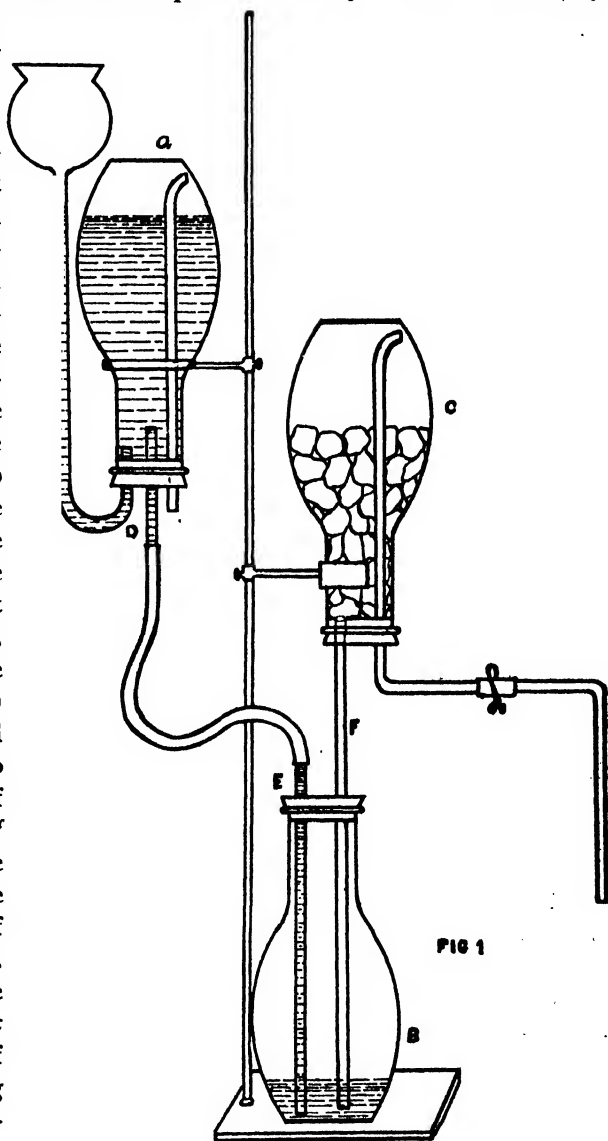


FIG 1

The stopper of bottle *c* is removed, carrying with it the stopper of bottle *b*. Bottle *c* is then filled with the necessary material and the stopper inserted. The other stopper is then inserted in bottle *b*. The clamp is then attached as shown.

The reservoir bottle is filled with the proper strength of acid by means of the thistle-tube. Opening the pinchcock forces acid up into the generating bottle, while closing the pinchcock drives acid automatically back into reservoir bottle. Since the upper end of tube *f* is level with the

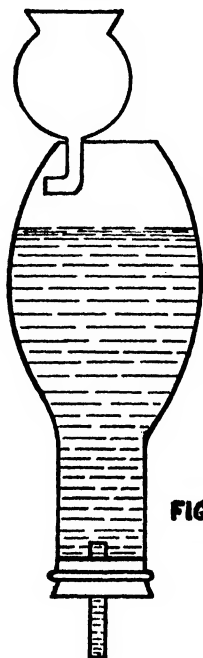


FIG 2

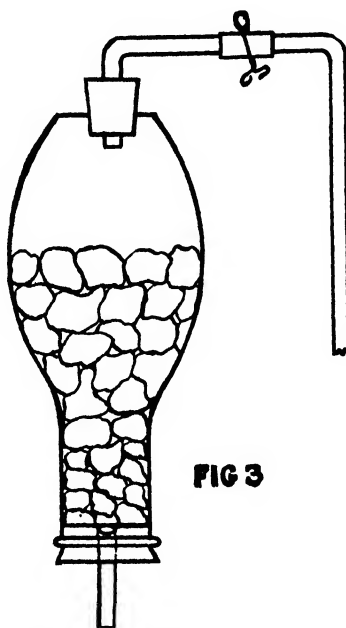


FIG 3

stopper, no acid remains in bottle *c*. To empty the generator of spent acid, detach bottle *b*, pour out the contents, replace the bottle and fill again.

Fig. 2 shows another type of reservoir bottle while Fig. 3 shows still another form. The use of gas bottles with openings in them can be substituted.

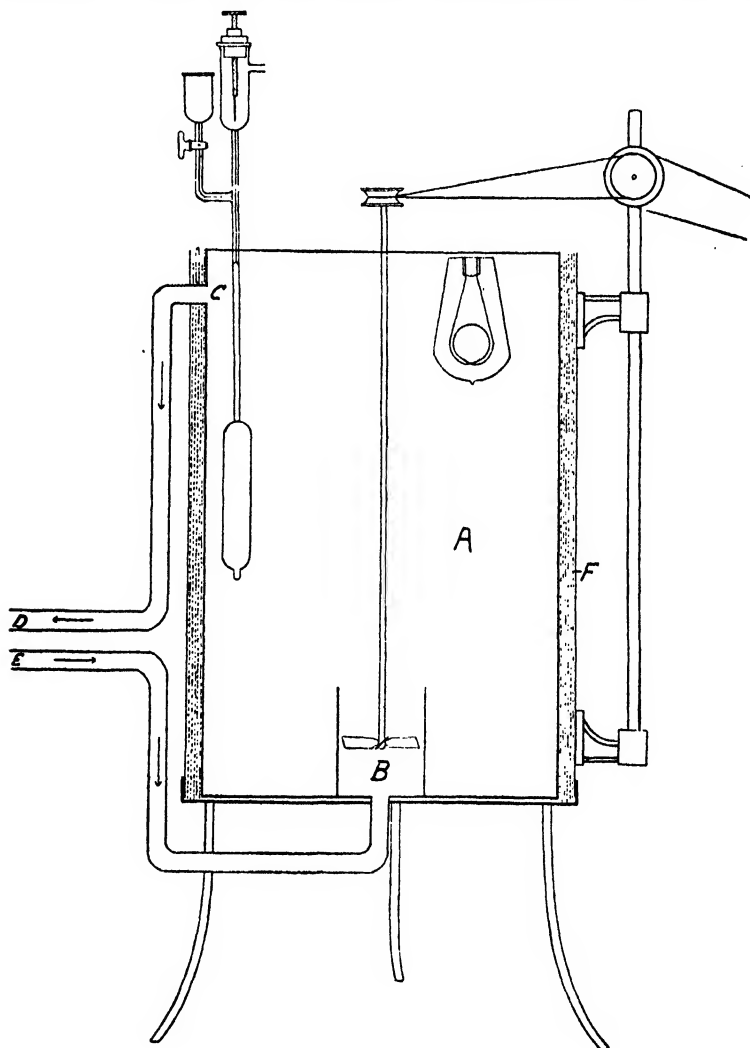
The unique advantages of this generator are:

1. Slight possibility of large pieces of material getting into the reservoir bottle and rapidly diluting the strength of the acid.
2. Rapid change as a generator for one gas to that of another by adding proper materials.
3. A regulating pressure device by sliding the reservoir bottle up and down the iron rod.
4. And finally, it is quickly constructed, portable, cheap and its capacity can be readily increased.

THEODORE COHEN.

An Improved Heating Apparatus for Maintaining Constant Temperatures in Work with Polarimeters and Refractometers.—In the course of some work upon the effect of temperature upon the specific rotation of optically active substances in solution, it was found necessary to maintain constant temperatures over long periods of time. The conditions demanded that the heating apparatus be one which is simple and convenient and at the same time one which permits the easy reproduction of any given temperature.

Various forms of apparatus devised for this purpose are described in the literature. Some of these consist in principle of a coil for running



water heated either by a Bunsen flame, or an electric coil. Where such methods are used in large crowded chemical laboratories the results obtained are unsatisfactory owing to fluctuations both in the gas and water pressures. Several modifications of this form were tried and discarded. While satisfactory as regards the regulation of temperature, the heating apparatus devised by Landolt for polarimeters is nevertheless inconvenient.

After several attempts the apparatus sketched in the accompanying diagram was perfected and the results obtained far exceeded our expectations.

In the figure, *A* is a round cylindrical vessel 25 cm. in diameter and 40 cm. in depth. Directly in the center and at the bottom of *A* is soldered the small cylinder, *B*, 62 cm. in diameter by 75 cm. in depth. Within the small cylinder rotates a motor-driven stirrer of propeller form. At *C*, slightly below the water level, is soldered a 9 mm. galvanized iron tube. A similar tube opening directly into the center of *B* is soldered to the bottom of the bath. The two open ends, *D*, *E*, are attached directly to the jacketed observation tube by means of short pieces of rubber tubing. Surrounding the bath is a layer, *F*, of felt or asbestos paper.

For temperatures near that of the ordinary laboratory temperature, the bath is heated by means of an immersed incandescent lamp and the temperature electrically controlled by means of a contact toluene regulator in series with a telegraph relay and battery. For temperatures considerably above that of the room, a second lamp is connected in parallel with the first. By applying the heat from a Bunsen burner the bath may be quickly heated and adjusted to any desired higher temperature. Owing to the presence of the small cylinder, *B*, the bath is equally adapted for use with ice at 0°, while for temperatures between 0° and that of the room a cooling coil connected with the water supply may be introduced.

When the bath is connected with the observation tube and the stirrer is driven at the rate of 500 to 600 r. p. m., the water circulates through the tube with an exceedingly high velocity. To judge of the force driving the water, it may be stated that when the tubes, *D*, *E*, are open and the stirrer is revolving at the above rate, the lifting power of the stirrer is sufficient to support a column of water eight inches in height. The speed with which the water is driven under hydrostatic equilibrium is, therefore, obvious. Under these conditions it is possible to maintain any desired temperature constant to $\pm 0.01^\circ$ — $\pm 0.02^\circ$ for any desired period of time.

Owing to the fact that the observation tube is of necessity at some distance from the bath, its temperature will be slightly lower and the difference will be greater, the higher the temperature to which the bath is heated. If the liquid in the observation tube must be at a definite temperature, the temperature of the bath can easily be adjusted so as to

produce the desired temperature and the temperature of the tube regulated with the same degree of constancy.

J. N. PEARCE.

PHYSICAL CHEMICAL LABORATORY,
THE STATE UNIVERSITY OF IOWA.

Measurement of the Vapor Pressures of Solutions.—In the December number of *THIS JOURNAL*¹ there is an article by Frazer and Lovelace on the measurement of vapor pressures of solutions by means of the Rayleigh manometer. A very similar method will be found described by me in *THIS JOURNAL* in 1908,² except that I employed the form of manometer devised by Morley.³ The principle of the two manometers is, however, the same, and the sensitiveness of one can be made fully equal to that of the other.

O. F. TOWER.

CLEVELAND, O.

[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY,
No. 243.]

THE ADDITION COMPOUNDS OF ALDEHYDES AND KETONES WITH ORGANIC ACIDS.

By JAMES KENDALL AND WILLIS A. GIBBONS.

Received November 14, 1914.

In the first article of this series,⁴ it has been shown that dimethylpyrone forms addition products with organic acids, and that these addition products are uniformly more stable the stronger the acid employed. The basic (unsaturated) properties of dimethylpyrone were regarded as due to the presence of the carbonyl group, $>C = O^+$, the compounds formed being oxonium salts. These views have been more fully developed in subsequent papers,⁵ and found to be consistent with the experimental results throughout.

In the present investigation the same problem is taken up from the reverse direction. The *acid* component of the system is kept constant, while the *basic* component, containing the typical carbonyl group, is made to vary. For the acid component trichloroacetic acid was selected, since in the previous work it has been found, as the strongest of the simple organic acids, to give the most stable compounds with substances containing unsaturated oxygen. For the basic component two substances were chosen as starting points: benzaldehyde, the simplest aromatic aldehyde, and acetophenone, the simplest aromatic ketone.⁶ The examination of the freezing-point curves of these substances with trichloroacetic

¹ 36, 2439 (1914).

² *THIS JOURNAL*, 30, 1219 (1908).

³ *Am. J. Sci.*, 13, 455 (1902).

⁴ Kendall, *THIS JOURNAL*, 36, 1222 (1914).

⁵ Kendall, *Ibid.*, 36, 1722 (1914); Kendall and Carpenter, *Ibid.*, 36, 2498 (1914).

⁶ Aliphatic aldehydes and ketones will be studied in a future communication.

acid showed that an equimolecular addition compound was formed in both cases. These compounds differed, however, from those obtained with dimethylpyrone and trichloroacetic acid in being very unstable and largely dissociated into their components on fusion. This was evidenced by the flatness of the maxima on the freezing-point curves.

The effect of the introduction of various groups, of acidic or basic nature, into these simple substances was now investigated. The presence of an *acidic* group in the nucleus should *decrease* the basic characteristics and consequently, according to the theory developed in the preceding articles, diminish the stability of the addition compounds produced, or even prevent the formation of addition products altogether. The effect of a *basic* group, on the other hand, should be to *increase* the tendency towards compound formation, and the isolation of more stable compounds should be expected. These rules were, indeed, found to hold throughout the investigation.

The method followed was substantially the same as has been described in the previous papers, to which reference must be made for the experimental details. The substances employed were, for the most part, Kahlbaum specimens, the purity of which was found to be sufficient for the purposes of the investigation by determination of the point of fusion.¹ In a few cases special methods of purification, however, were adopted.

It has, of course, long been known that aldehydes and ketones form addition compounds of unstable nature with acids, but the investigations previously carried out have always been by the direct organic method—admixture of the components and analysis by combustion of the compound isolated. The freezing-point method has been employed in no single case of the type considered in this paper, except by Maass and McIntosh² for acetone and hydrochloric acid. The advantages of this method are, however, sufficient to recommend its more general adoption. It indicates at once all compounds formed between the two components, analysis is not necessary (since the composition of any addition product is read directly from the curve), and the relative stability of the compounds isolated is also established.

The following aldehydes and ketones were investigated with trichloroacetic acid. (In the case of the aldehydes, the dissociation constants of the corresponding acids³ are appended, to illustrate the acidic or basic character of the substituted group.)

¹ Trichloroacetic acid is extremely hygroscopic, and the last traces of water are removed only by prolonged desiccation over sulfuric acid. The melting points of the samples employed varied from 57.3° to 57.9°.

² Maass and McIntosh, *THIS JOURNAL*, 34, 1286 (1912).

³ Ostwald, *Z. physik. Chem.*, 3, 418 (1889).

| Aldehydes. | 100 K. <i>acid</i> . | Ketones. |
|----------------------------------|----------------------|----------------------|
| Benzaldehyde..... | 0.0060 | Acetophenone |
| Salicylic aldehyde..... | 0.102 | Benzophenone |
| <i>m</i> -Oxybenzaldehyde..... | 0.0087 | Phenyl anisyl ketone |
| <i>p</i> -Oxybenzaldehyde..... | 0.00286 | Benzil |
| <i>o</i> -Nitrobenzaldehyde..... | 0.616 | Benzoquinone |
| <i>m</i> -Nitrobenzaldehyde..... | 0.0345 | Dibenzalacetone |
| <i>p</i> -Nitrobenzaldehyde..... | 0.0396 | |
| Anisaldehyde..... | 0.0032 | |
| Vanillin..... | 0.00298 | |
| Piperonal..... | 0.0033 | |

A few of the above substances were also investigated with chloroacetic acid and benzoic acid. In no case, however, was any indication of compound formation with these weaker acids obtained. This is again in accordance with previous experimental results.¹

For purposes of comparison, a list of compounds of the type acid—aldehyde (or ketone) recorded by earlier investigators is given below. Only those aldehydes and ketones investigated in this paper (or previous papers of this series) are included, and the compounds obtained are indicated by condensed formulae (A = aldehyde or ketone, B = acid).

| System. | Compounds. | Observer. |
|---|---|--------------------------------------|
| Benzaldehyde-HCl(HBr) | AB | Vorländer ² |
| <i>p</i> -Hydroxybenzaldehyde-HBr | AB | Gomberg and Cone ³ |
| Anisaldehyde-HCl | AB; AB ₂ | Vorländer ² |
| Anisaldehyde-HBr | AB | Vorländer |
| Vanillin-HBr | AB | Gomberg and Cone ³ |
| Vanillin-H ₂ SO ₄ | AB | Hoogewerff and van Dorp ⁴ |
| Piperonal-HCl | AB; AB ₂ | Vorländer ² |
| Piperonal-HBr | AB | Vorländer |
| Piperonal-H ₂ SO ₄ | A ₂ B ₃ | Hoogewerff and van Dorp ⁴ |
| Acetophenone-H ₂ SO ₄ | A ₂ B | Kendall and Carpenter ⁵ |
| Benzophenone-H ₂ SO ₄ | AB | Kendall and Carpenter |
| Benzil-H ₂ SO ₄ | AB | Hoogewerff and van Dorp ⁴ |
| Dibenzalacetone-HCl | AB; AB ₂ | Thiele and Straus ⁶ |
| Dibenzalacetone-CCl ₃ .COOH | AB | Stobbe ⁷ |
| Dimethylpyrone-HCl | AB; AB ₂ | Gomberg and Cone ³ |
| Dimethylpyrone-HBr | AB; AB ₂ ; AB ₄ | McIntosh ⁸ |
| Dimethylpyrone-H ₂ SO ₄ | A ₂ B; AB; A ₂ B ₂ | Kendall and Carpenter ⁵ |
| Dimethylpyrone-CCl ₃ .COOH | AB; AB ₂ | Kendall ⁹ |

¹ Kendall, *THIS JOURNAL*, 36, 1722 (1914).

² Vorländer, *Ann.*, 341, 1 (1905).

³ Gomberg and Cone, *Ibid.*, 376, 183 (1911).

⁴ Hoogewerff and van Dorp, *Rec. trav. chim. Pays Bas*, 21, 353 (1902).

⁵ Kendall and Carpenter, *THIS JOURNAL*, 36, 2498 (1914).

⁶ Thiele and Strauss, *Ber.*, 36, 2375 (1903).

⁷ Stobbe, *Ann.*, 370, 93 (1909).

⁸ McIntosh, *THIS JOURNAL*, 32, 542 (1910).

⁹ Kendall, *Ibid.*, 36, 1222 (1914).

It may be mentioned here that, in the past, the main investigations upon systems of this type have been in a special field, having as their object the examination of the behavior of α,β -unsaturated ketones with acids. This point will be discussed briefly later, in connection with the results obtained with dibenzalacetone.

The results of the present article are collected in the tables given below; these are arranged as in preceding papers. (T = temperature of *incipient* solidification.) A few typical freezing-point curves are shown in the accompanying diagram.

Aldehydes.

1. Benzaldehyde-Trichloroacetic Acid.—The equimolecular addition product $C_6H_5.CHO, CCl_3.COOH$ was obtained, m. p. 8.4° , stable at its maximum. The compound separates in the form of beautiful colorless needles from a deep orange-pink solution. The system could not be completely investigated, since mixtures containing a large excess of benzaldehyde oxidize rapidly during the course of experiment, and finally deposit crystals of benzoic acid at the low temperatures involved. The freezing points given below were obtained with the use of a freshly-opened "special K" Kahlbaum sample of benzaldehyde, the work being carried through as rapidly as possible.

(a) Solid phase, $CCl_3.COOH$.

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 100 | 91.5 | 83.8 | 75.2 | 69.1 | 63.8 |
| T..... | 57.3 | 51.3 | 44.7 | 33.1 | 21.0 | 4.3 |

(b) Solid phase, $C_6H_5.CHO, CCl_3.COOH$.

| | | | | | | | |
|------------|------|------|------|------|------|------|------|
| % acid.... | 61.1 | 55.6 | 50.0 | 45.4 | 40.0 | 34.3 | 29.4 |
| T..... | 3.6 | 7.1 | 8.4 | 7.2 | 4.3 | -0.8 | -6.9 |

2. Salicylic Aldehyde-Trichloroacetic Acid.—This system also could not be completely investigated, since mixtures containing excess of aldehyde formed, on cooling, a viscous, glassy mass from which no crystallization could be obtained. No compound formation was indicated in the region examined. It is probable that the presence of the hydroxyl group in the ortho position decreases the basic characteristics of the aldehyde sufficiently to prevent combination occurring. (See list, on page 151, of acidic strengths.)

(a) Solid phase, $CCl_3.COOH$.

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 100 | 91.8 | 83.6 | 74.2 | 63.4 | 55.1 |
| T..... | 57.9 | 52.4 | 44.1 | 32.2 | 13.4 | -6.9 |

3. *m*-Hydroxybenzaldehyde-Trichloroacetic Acid.—The hydroxyl group in the meta position is weakly acidic; no compound formation was indicated.

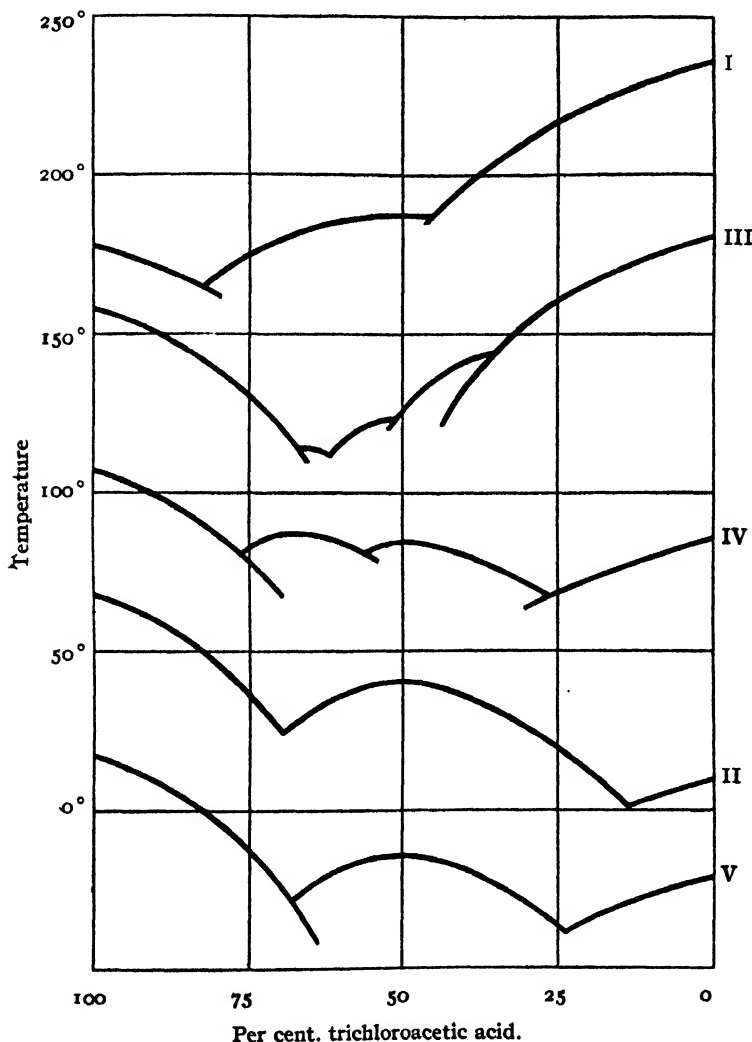
(a) Solid phase, $CCl_3.COOH$.

| | | | | | |
|------------|------|------|------|------|------|
| % acid.... | 100 | 92.7 | 85.6 | 79.9 | 72.7 |
| T..... | 57.9 | 52.6 | 46.3 | 39.9 | 30.3 |

(b) Solid phase, $C_6H_4(OH).CHO$.

| | | | | | | | |
|------------|------|------|------|------|------|------|-------|
| % acid.... | 65.8 | 59.7 | 49.1 | 37.6 | 25.5 | 14.8 | 0 |
| T..... | 24.2 | 39.3 | 59.6 | 75.9 | 88.9 | 98.5 | 107.4 |

4. *p*-Hydroxybenzaldehyde-Trichloroacetic Acid.—In the *p*-position the hydroxyl group is *basic* in its effect, consequently compound formation should be expected. The components form, on admixture, a delicate pink solution, and the freezing-point curve indicates an equimolecular compound, m. p. 67.8° , stable at its maximum. (See diagram.)



- I. *p*-Oxybenzaldehyde Subtract 120° from temperature scale.
- II. Anisaldehyde. Subtract 10° from temperature scale.
- III. Vanillin. Subtract 100° from temperature scale.
- IV. Piperonal. Subtract 50° from temperature scale.
- V. Acetophenone. Add 40° to temperature scale.

(a) Solid phase, CCl_3COOH .

| | | | | |
|------------|------|------|------|------|
| % acid.... | 100 | 94.0 | 86.7 | 79.7 |
| T..... | 57.9 | 54.6 | 48.8 | 41.9 |

(b) Solid phase, $\text{C}_6\text{H}_4\text{OH.CHO}$, CCl_3COOH .

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 79.7 | 72.8 | 66.2 | 61.3 | 52.8 | 46.0 |
| T..... | 49.7 | 57.7 | 62.7 | 65.5 | 67.5 | 67.1 |

(c) Solid phase, $\text{C}_6\text{H}_4\text{OH.CHO}$.

| | | | | | | |
|------------|------|------|------|-------|-------|-------|
| % acid.... | 46.0 | 38.0 | 29.9 | 20.4 | 9.9 | 0 |
| T..... | 65.9 | 79.6 | 90.9 | 101.5 | 109.6 | 115.6 |

5. *o*-Nitrobenzaldehyde-Trichloroacetic Acid.—The nitro group increases the acidic strength in all positions. In accordance with this, it was found that the introduction of the nitro group into benzaldehyde deprives it of its basic properties, and no compounds were isolated in any of the three following systems:

(a) Solid phase, CCl_3COOH .

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 100 | 90.8 | 82.2 | 73.3 | 64.4 | 55.2 |
| T..... | 57.3 | 52.9 | 46.5 | 38.2 | 27.8 | 13.5 |

(b) Solid phase, $\text{C}_6\text{H}_4\text{NO}_2\text{CHO}$.

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 49.5 | 41.6 | 31.4 | 20.2 | 11.1 | 0 |
| T..... | 5.6 | 16.1 | 26.3 | 33.4 | 37.8 | 42.9 |

6. *m*-Nitrobenzaldehyde-Trichloroacetic Acid.(a) Solid phase, CCl_3COOH .

| | | | | | | | |
|------------|------|------|------|------|------|------|------|
| % acid.... | 100 | 91.0 | 83.9 | 77.4 | 70.2 | 62.3 | 54.4 |
| T..... | 57.3 | 51.6 | 46.1 | 39.8 | 31.6 | 20.4 | 6.0 |

(b) Solid phase, $\text{C}_6\text{H}_4\text{NO}_2\text{CHO}$.

| | | | | | | | |
|------------|------|------|------|------|------|------|------|
| % acid.... | 54.4 | 47.8 | 39.0 | 30.4 | 20.3 | 11.9 | 0 |
| T..... | 14.0 | 21.7 | 29.8 | 37.7 | 45.4 | 49.9 | 55.7 |

7. *p*-Nitrobenzaldehyde-Trichloroacetic Acid.(a) Solid phase, CCl_3COOH .

| | | | | |
|------------|------|------|------|------|
| % acid.... | 100 | 91.4 | 84.1 | 75.7 |
| T..... | 57.3 | 52.2 | 46.0 | 37.4 |

(b) Solid phase, $\text{C}_6\text{H}_4\text{NO}_2\text{CHO}$.

| | | | | | | | | |
|------------|------|------|------|------|------|------|------|-------|
| % acid.... | 65.5 | 59.3 | 52.5 | 44.6 | 35.3 | 21.9 | 12.2 | 0 |
| T..... | 33.6 | 46.0 | 57.3 | 68.2 | 78.3 | 90.7 | 97.4 | 104.4 |

8. Anisaldehyde-Trichloroacetic Acid.—Here the presence of the methoxyl group increases the *basic* characteristics of the aldehyde, and compound formation should be expected. The components give, on admixture, a deep red solution, from which colorless crystals of the addition product $\text{C}_6\text{H}_4\text{OCH}_3\text{CHO}$, CCl_3COOH are deposited on freezing. The compound is stable at its maximum, and melts at 30.9° . (See diagram.)

(a) Solid phase, CCl_3COOH .

| | | | | | |
|------------|------|------|------|------|------|
| % acid.... | 100 | 90.2 | 80.9 | 72.8 | 69.8 |
| T..... | 57.9 | 50.0 | 37.7 | 22.2 | 14.5 |

(b) Solid phase, $C_6H_4OCH_3.CHO$, $CCl_3.COOH$.

| | | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|------|
| % acid.... | 69.8 | 67.6 | 61.8 | 55.3 | 48.7 | 41.8 | 35.1 | 27.1 | 18.8 |
| T..... | 14.5 | 17.9 | 24.4 | 29.4 | 30.7 | 27.7 | 21.9 | 12.6 | 0.3 |

(c) Solid phase, $C_6H_4OCH_3.CHO$.

| | | | |
|------------|------|------|------|
| % acid.... | 12.0 | 6.8 | 0 |
| T..... | -8.1 | -4.9 | -0.9 |

9. Vanillin-Trichloroacetic Acid.—In vanillin there has been introduced into the benzaldehyde nucleus a methoxyl group in the *m*-position and a hydroxyl group in the *p*-position; both groups exert a basic influence. The tendency towards compound formation, therefore, should be considerably increased. The components give, on fusion together, a dark red solution, and an examination of the freezing-point curve of the system shows that *three* addition products are formed:

- (1) $C_6H_3OH.OCH_3.CHO$, $2CCl_3.COOH$, stable at its maximum, m. p. 14.3° .
- (2) $C_6H_3OH.OCH_3.CHO$, $CCl_3.COOH$, unstable at its maximum, m. p. 23.0° (by extrapolation).
- (3) $2C_6H_3OH.OCH_3.CHO$, $CCl_3.COOH$, unstable at its maximum, m. p. 45.0° (by extrapolation).

Investigation of the system is rendered difficult by persistent supercooling and by the dark color of the solutions. The freezing-point curve is shown in the annexed diagram.

(a) Solid phase, $CCl_3.COOH$.

| | | | | | | | |
|------------|------|------|------|------|------|------|------|
| % acid.... | 100 | 91.4 | 84.0 | 77.6 | 72.3 | 66.4 | 65.6 |
| T..... | 57.3 | 51.7 | 44.5 | 35.0 | 25.5 | 12.0 | 10.3 |

(b) Solid phase, $C_6H_3OH.OCH_3.CHO$, $2CCl_3.COOH$.

| | | | |
|------------|------|------|------|
| % acid.... | 66.0 | 64.4 | 62.7 |
| T..... | 14.2 | 13.8 | 12.8 |

(c) Solid phase, $C_6H_3OH.OCH_3.CHO$, $CCl_3.COOH$.

| | | | | | |
|------------|------|------|------|------|------|
| % acid.... | 60.8 | 58.8 | 58.2 | 56.3 | 54.0 |
| T..... | 14.6 | 17.8 | 18.0 | 21.2 | 22.0 |

(d) Solid phase, $2C_6H_3OH.OCH_3.CHO$, $CCl_3.COOH$.

| | | | | | | | |
|------------|------|------|------|------|------|------|------|
| % acid.... | 52.1 | 48.8 | 43.6 | 43.4 | 41.3 | 39.2 | 35.3 |
| T..... | 21.0 | 28.0 | 37.2 | 37.8 | 40.0 | 41.7 | 44.5 |

(e) Solid phase, $C_6H_3OH.OCH_3.CHO$.

| | | | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|------|------|
| % acid.... | 43.6 | 37.8 | 35.3 | 31.5 | 25.4 | 22.4 | 17.5 | 13.3 | 6.3 | 0 |
| T..... | 21.0 | 39.3 | 44.5 | 50.5 | 60.1 | 63.3 | 68.2 | 71.7 | 76.6 | 80.9 |

10. Vanillin-Chloroacetic Acid.—With this relatively very weak acid vanillin exhibits no tendency to form addition products.

(a) Solid phase, $CH_2Cl.COOH$.

| | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|
| % acid.... | 100 | 93.0 | 88.7 | 80.4 | 74.8 | 69.2 | 61.5 | 57.8 |
| T..... | 61.4 | 57.6 | 54.0 | 48.8 | 44.0 | 39.0 | 34.0 | 30.8 |

(b) Solid phase, $C_6H_3OH.OCH_3.CHO$.

| | | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|------|
| % acid.... | 51.6 | 49.7 | 45.6 | 39.4 | 33.7 | 28.2 | 20.4 | 10.9 | 0 |
| T..... | 39.2 | 42.0 | 47.3 | 53.3 | 59.0 | 63.4 | 69.0 | 74.3 | 80.9 |

11. Piperonal-Trichloroacetic Acid.—Here again the introduction of a group of basic nature, $\text{CH}_2 \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array}$, into the benzaldehyde nucleus was found

to be accompanied by an increase in the tendency to form addition products with acids. With trichloroacetic acid piperonal forms *two* compounds

(1) $\text{C}_8\text{H}_6\text{O}_3$, $2\text{CCl}_3\text{COOH}$, stable at its maximum, m. p. 37.4° .

(2) $\text{C}_8\text{H}_6\text{O}_3$, CCl_3COOH , stable at its maximum, m. p. 35.0° .

The freezing-point curve of the system is given in the diagram.

(a) Solid phase, CCl_3COOH .

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 100 | 90.3 | 82.4 | 76.3 | 75.5 | 69.8 |
| T..... | 57.3 | 49.7 | 40.1 | 30.8 | 29.3 | 17.5 |

(b) Solid phase, $\text{C}_8\text{H}_6\text{O}_3$, $2\text{CCl}_3\text{COOH}$.

| | | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|------|
| % acid.... | 76.3 | 74.4 | 72.2 | 68.7 | 67.3 | 65.2 | 64.4 | 59.0 | 54.0 |
| T..... | 30.8 | 33.5 | 36.2 | 37.3 | 37.4 | 36.9 | 36.1 | 33.3 | 29.0 |

(c) Solid phase, $\text{C}_8\text{H}_6\text{O}_3$, CCl_3COOH .

| | | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|------|
| % acid.... | 53.5 | 51.0 | 50.3 | 48.3 | 43.5 | 39.4 | 35.3 | 33.0 | 25.2 |
| T..... | 33.2 | 34.9 | 35.0 | 34.8 | 32.7 | 29.9 | 26.8 | 24.8 | 18.7 |

(d) Solid phase, $\text{C}_8\text{H}_6\text{O}_3$.

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 30.0 | 28.1 | 25.2 | 17.3 | 11.6 | 0 |
| T..... | 13.7 | 16.2 | 18.7 | 24.4 | 28.7 | 35.5 |

12. Piperonal-Chloroacetic Acid.—Piperonal gives no indication of compound formation with this weaker acid (compare 10).

(a) Solid phase, $\text{CH}_2\text{Cl.COOH}$.

| | | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|------|
| % acid.... | 100 | 91.7 | 84.9 | 78.9 | 73.6 | 69.0 | 65.1 | 60.4 | 52.9 |
| T..... | 61.4 | 56.6 | 52.2 | 47.2 | 42.4 | 37.5 | 33.0 | 28.4 | 22.0 |
| % acid.... | 49.7 | 44.3 | 39.7 | | | | | | |
| T..... | 17.8 | 14.5 | 10.2 | | | | | | |

(b) Solid phase, $\text{C}_8\text{H}_6\text{O}_3$.

| | | | | | |
|------------|------|------|------|------|------|
| % acid.... | 35.8 | 26.8 | 19.3 | 8.2 | 0 |
| T..... | 11.0 | 18.7 | 23.8 | 31.0 | 35.5 |

13. Piperonal-Benzoic Acid.—In this system again no compound formation was indicated.

(a) Solid phase, $\text{C}_6\text{H}_5\text{COOH}$.

| | | | | | | | | | |
|------------|-------|-------|-------|-------|------|------|------|------|------|
| % acid.... | 100 | 86.2 | 80.6 | 73.1 | 65.5 | 59.2 | 50.0 | 44.2 | 37.4 |
| T..... | 121.4 | 111.0 | 106.6 | 100.8 | 94.2 | 89.0 | 81.0 | 74.2 | 65.5 |
| % acid.... | 30.0 | 25.9 | 22.1 | 18.7 | | | | | |
| T..... | 54.6 | 48.4 | 39.7 | 32.0 | | | | | |

(b) Solid phase, $\text{C}_8\text{H}_6\text{O}_3$.

| | | | | |
|------------|------|------|------|------|
| % acid.... | 18.5 | 17.0 | 10.2 | 0 |
| T..... | 27.2 | 27.4 | 30.8 | 35.5 |

14. Nitropiperonal-Trichloroacetic Acid.—The introduction of the acidic nitro group into piperonal results in the loss of its basic properties, and no compound formation with trichloroacetic acid is obtained.

(a) Solid phase, CCl_3COOH .

| | | | | | |
|------------|------|------|------|------|------|
| % acid.... | 100 | 91.0 | 82.9 | 74.4 | 66.8 |
| T..... | 57.9 | 52.3 | 45.4 | 37.3 | 28.9 |

(b) Solid phase, $\text{C}_6\text{H}_5\text{O}_2\text{NO}_2$.

| | | | | | | | |
|------------|------|------|------|------|------|------|------|
| % acid.... | 66.8 | 57.0 | 48.4 | 38.0 | 26.1 | 14.5 | 0 |
| T..... | 32.9 | 46.1 | 55.9 | 66.2 | 76.9 | 85.7 | 94.1 |

Ketones.

15. Acetophenone-Trichloroacetic Acid.—The equimolecular addition product, $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_3$, CCl_3COOH was obtained, stable at its maximum, m. p. 26.0° . (See diagram.)

(a) Solid phase, CCl_3COOH .

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 100 | 91.4 | 83.8 | 78.1 | 72.0 | 63.8 |
| T..... | 57.3 | 50.5 | 41.9 | 33.3 | 21.3 | —2.2 |

(b) Solid phase, $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_3$, CCl_3COOH .

| | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|
| % acid.... | 63.8 | 58.3 | 52.1 | 48.4 | 43.0 | 36.5 | 30.7 | 25.1 |
| T..... | 17.9 | 22.9 | 25.6 | 25.7 | 23.3 | 18.1 | 11.6 | 3.7 |

(c) Solid phase, $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_3$.

| | | | | |
|------------|------|------|------|------|
| % acid.... | 19.9 | 14.5 | 8.4 | 0 |
| T..... | 5.1 | 10.1 | 14.4 | 18.7 |

16. Acetophenone-Chloroacetic Acid.—With this weaker acid acetophenone exhibits no tendency towards compound formation.

(a) Solid phase, $\text{CH}_2\text{Cl}\cdot\text{COOH}$.

| | | | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|------|------|
| % acid.... | 100 | 85.4 | 81.8 | 78.7 | 74.2 | 69.7 | 66.6 | 59.0 | 50.0 | 40.1 |
| T..... | 61.4 | 51.1 | 47.6 | 44.7 | 40.5 | 35.7 | 32.7 | 22.2 | 7.6 | —8.8 |

(b) Solid phase, $\text{C}_6\text{H}_5\text{CO}\cdot\text{CH}_3$.

| | | | | | |
|------------|------|------|------|------|------|
| % acid.... | 36.1 | 25.0 | 19.3 | 6.8 | 0 |
| T..... | —3.8 | 5.0 | 8.0 | 15.5 | 18.7 |

17. Benzophenone-Trichloroacetic Acid.—This system could not be completely examined owing to the persistent supercooling of the solutions to a hard, glassy mass without crystallization. The form of the freezing-point curve¹ indicates the presence of a compound in solution; no addition product, however, could be isolated.

(a) Solid phase, CCl_3COOH .

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 100 | 89.7 | 81.4 | 74.5 | 68.6 | 62.5 |
| T..... | 57.3 | 49.7 | 40.3 | 28.5 | 16.2 | 0.4 |

(b) Solid phase, $\text{C}_6\text{H}_5\text{CO}\cdot\text{C}_6\text{H}_5$.

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 41.6 | 36.6 | 28.4 | 22.4 | 13.9 | 0 |
| T..... | —1.0 | 10.1 | 22.4 | 30.2 | 38.2 | 46.3 |

18. Phenyl Anisyl Ketone-Trichloroacetic Acid.—Here again complete investigation of the system was impossible, the mixtures cooling to a glassy mass without crystallization. The presence of an addition compound in solution, however, could be inferred from the form of the curves and from the bright red color of the mixtures.

¹ See Kendall, *THIS JOURNAL*, 36, 1733 (1914).

(a) Solid phase, CCl_3COOH .

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 100 | 92.9 | 86.9 | 80.6 | 74.4 | 67.8 |
| T..... | 57.9 | 52.4 | 44.8 | 34.5 | 22.5 | 4.3 |

(b) Solid phase, $\text{C}_6\text{H}_5\text{CO.C}_6\text{H}_4\text{OCH}_3$.

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 45.5 | 35.2 | 28.0 | 20.3 | 13.0 | 0 |
| T..... | 7.4 | 31.7 | 41.3 | 48.2 | 53.0 | 58.7 |

19. Benzil-Trichloroacetic Acid.—In this system no compound was isolated. The weaker acids, chloroacetic and benzoic, also give no indication of compound formation with benzil (see 20 and 21, below).

(a) Solid phase, CCl_3COOH .

| | | | | | |
|------------|------|------|------|------|------|
| % acid.... | 100 | 91.4 | 81.2 | 75.8 | 69.9 |
| T..... | 57.3 | 50.9 | 39.8 | 31.3 | 21.5 |

(b) Solid phase, $\text{C}_6\text{H}_5\text{CO.CO.C}_6\text{H}_5$.

| | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|
| % acid.... | 62.0 | 54.4 | 47.5 | 39.5 | 30.4 | 22.0 | 12.2 | 0 |
| T..... | 31.2 | 45.0 | 55.3 | 65.3 | 73.8 | 80.8 | 87.0 | 94.0 |

20. Benzil-Chloroacetic Acid.(a) Solid phase, $\text{CH}_2\text{Cl.COOH}$.

| | | | |
|------------|------|------|------|
| % acid.... | 100 | 90.0 | 80.2 |
| T..... | 61.4 | 56.3 | 51.6 |

(b) Solid phase, $\text{C}_6\text{H}_5\text{CO.CO.C}_6\text{H}_5$.

| | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|
| % acid.... | 67.1 | 57.8 | 43.6 | 34.2 | 18.0 | 13.0 | 9.9 | 0 |
| T..... | 58.3 | 65.3 | 74.0 | 79.0 | 86.6 | 88.6 | 89.9 | 94.0 |

21. Benzil-Benzoic Acid.(a) Solid phase, $\text{C}_6\text{H}_5\text{COOH}$.

| | | | | | | |
|------------|-------|-------|-------|------|------|------|
| % acid.... | 100 | 86.2 | 75.1 | 66.8 | 53.8 | 45.4 |
| T..... | 121.4 | 111.5 | 104.9 | 98.3 | 88.5 | 81.7 |

(b) Solid phase, $\text{C}_6\text{H}_5\text{CO.CO.C}_6\text{H}_5$.

| | | | | | |
|------------|------|------|------|------|------|
| % acid.... | 36.2 | 25.8 | 19.4 | 9.9 | 0 |
| T..... | 79.5 | 83.1 | 86.6 | 90.8 | 94.0 |

22. Benzoquinone-Trichloroacetic Acid.—No compound formation was indicated in this system.

(a) Solid phase, CCl_3COOH .

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 100 | 91.7 | 84.7 | 77.3 | 70.5 | 62.2 |
| T..... | 57.9 | 52.1 | 44.9 | 34.4 | 22.2 | 2.6 |

(b) Solid phase, $\text{C}_6\text{H}_4\text{O}_2$.

| | | | | | | | |
|------------|------|------|------|------|------|-------|-------|
| % acid.... | 55.0 | 46.9 | 39.8 | 29.9 | 20.9 | 11.5 | 0 |
| T..... | 24.6 | 48.3 | 63.9 | 81.4 | 94.6 | 105.1 | 114.6 |

23. Dibenzalacetone-Trichloroacetic Acid.—In this system *two* compounds were isolated:

- (1) $\text{C}_{17}\text{H}_{14}\text{O}$, $2\text{CCl}_3\text{COOH}$, unstable at its maximum, m. p. 86.5° (by extrapolation).
- (2) $\text{C}_{17}\text{H}_{14}\text{O}$, CCl_3COOH ,¹ stable at its maximum, m. p. 117.0° .

¹ Compare Stobbe, *Ann.*, 370, 93 (1909).

Investigation of the freezing-point curve is rendered difficult by the dark red color of the solutions. In mixtures containing excess of dibenzalacetone, also, decomposition begins to take place at the point of fusion; the system could, therefore, not be completely examined.

(a) Solid phase, CCl_3COOH .

| | | |
|------------|------|------|
| % acid.... | 100 | 93.0 |
| T..... | 57.3 | 48.3 |

(b) Solid phase, $\text{C}_{17}\text{H}_{14}\text{O}$, $2\text{CCl}_3\text{COOH}$.

| | | | | | | | | |
|------------|------|------|------|------|------|------|------|------|
| % acid.... | 89.0 | 87.5 | 86.3 | 83.6 | 81.3 | 79.0 | 76.5 | 71.5 |
| T..... | 51.6 | 58.1 | 61.9 | 70.0 | 73.8 | 78.3 | 82.6 | 85.2 |

(c) Solid phase, $\text{C}_{17}\text{H}_{14}\text{O}$, CCl_3COOH .

| | | | | | | | | | | | |
|------------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| % acid.... | 75.3 | 71.4 | 68.5 | 62.9 | 60.6 | 57.0 | 54.4 | 51.5 | 50.0 | 45.0 | 40.2 |
| T..... | 87.0 | 97.8 | 102.8 | 110.2 | 112.2 | 114.5 | 115.2 | 116.6 | 117.0 | 115.0 | 112.0 |

24. Dibenzalacetone-Chloroacetic Acid.—With this weaker acid dibenzalacetone gives no indication of compound formation. Decomposition again prevented a complete examination.

(a) Solid phase, CH_2ClCOOH .

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 100 | 92.7 | 86.3 | 82.0 | 77.3 | 72.3 |
| T..... | 61.4 | 56.5 | 50.5 | 46.2 | 41.5 | 36.1 |

(b) Solid phase, $\text{C}_{17}\text{H}_{14}\text{O}$.

| | | | | | | |
|------------|------|------|------|------|------|------|
| % acid.... | 68.4 | 65.0 | 61.9 | 58.7 | 53.6 | 49.3 |
| T..... | 33.0 | 42.9 | 51.0 | 58.0 | 67.0 | 74.0 |

Consideration of Results.

Ten aldehydes and six ketones have been examined with trichloroacetic acid. Five of the aldehydes gave no addition products; from the remaining five systems eight compounds were isolated. These were constituted as follows: (A = aldehyde, B = acid);

(a) 1 of the type A_2B .

(b) 5 of the type AB .

(c) 2 of the type AB_2 .

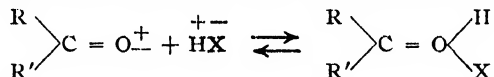
Of the six ketones, four gave no addition products. From the remaining two systems three compounds were isolated—two of the type AB , one of the type AB_2 . From systems containing an aldehyde (or ketone) and an acid weaker than trichloroacetic, no addition compounds could be obtained.

Compound formation, therefore, is dependent upon the strength of the acid employed—a fact already established in preceding papers. It is also directly dependent upon the acidic or basic nature of the groups included in the aldehyde or ketone. In the former class of substances, benzaldehyde gives a very unstable addition product with trichloroacetic acid. The presence of an *acidic* group in the nucleus causes such a decrease in the tendency towards compound formation that in no single case examined was an addition product obtained. On the other hand,

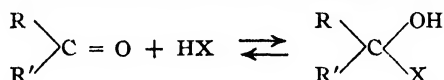
the presence of a *basic* group increases the tendency towards compound formation, and addition products of a more stable character were isolated.

These rules are not so clearly illustrated by the results obtained with ketones, owing to difficulties in the complete examination of the systems considered. Another regularity, however, is still present here—the color change on admixture of the components is uniformly greater, the more basic the group introduced.¹ Acetophenone, for example, gives with trichloroacetic acid a light yellow solution; phenyl anisyl ketone shows a more pronounced, reddish pink coloration. Similarly, in the case of aldehydes, *o*-nitrobenzaldehyde and trichloroacetic acid form an almost colorless solution, benzaldehyde gives an orange-pink coloration, anisaldehyde a deep red.

This color change has been attributed by Vorländer and Mumme² to a change in the degree of saturation of one or more elements composing the substances present. The variation in the tendency towards compound formation with the acidic and basic strengths of the two components has also been explained, in the preceding papers of this series, on the assumption that the compounds formed are *oxonium salts*. In the systems here investigated, the aldehyde or ketone is to be regarded as the ionizing medium (characteristically unsaturated), and the formation of an equimolecular compound may be expressed as follows:



According to Gomberg and Cone,³ the reaction proceeds quite differently, and the addition compounds formed are *carbonium salts*, *e. g.*:



The arguments in favor of the oxonium structure have already been discussed in full in previous articles, and need only brief recapitulation here. The following points are of importance:

(a) The *instantaneous* nature of the reaction, indicating its *ionic* character. Carbonium salt formation from an aldehyde or ketone cannot be expressed as a simple ionic reaction, but involves also the disruption of the carbonyl linkage. Analogous reactions of this type (*e. g.*, the addition of hydrocyanic acid or alkaline bisulfites) are time reactions.⁴

(b) The regular dependence of compound formation upon the acidic and basic strengths of the two components. This regularity is evident

¹ Compare Kendall, *THIS JOURNAL*, 36, 1242 (1914).

² *Ber.*, 36, 1470 (1903).

³ Gomberg and Cone, *Ann.*, 376, 183 (1911).

⁴ Stewart, *J. Chem. Soc.*, 87, 185 (1905).

not only in the formation or nonformation of compounds, but also in the relative stability of the addition product obtained. It does not seem probable that the formation of compounds should depend upon acidic and basic strengths unless the reaction were directly ionic.

(c) The isolation of compounds, other than equimolecular, which cannot be represented according to the carbonium hypothesis. Of the twenty-seven compounds listed on page 151, eleven have not the simple equimolecular formula; of the eleven compounds isolated in the present investigation, four are not equimolecular.

In conclusion here, the behavior of α,β -unsaturated ketones with acids may be briefly discussed. Dibenzalacetone, $\text{C}_6\text{H}_5\text{CH} : \text{CH}.\text{CO}.\text{CH} : \text{CH}.\text{C}_6\text{H}_5$ (see 23 and 24 above) has been the subject of frequent investigation in this connection.

Claisen and Ponder¹ first recorded the fact that dibenzalacetone gives an unstable addition product with hydrochloric acid. Baeyer and Villiger,² attempting to determine the constitution of this compound, noted that it was colored intensely red. If addition had taken place through the ethylene bonds, and the compound was a chlorohydrin, then the corresponding dichloride should also be red colored. Examination showed, however, that the dichloride was colorless, consequently the deduction was made that the addition product was an oxonium salt, addition of acid taking place on the carbonyl group.

Baeyer and Villiger assumed that the compound was equimolecular, $\text{C}_{17}\text{H}_{14}\text{O}$, HCl , but Vorländer and Mumme³ found that its composition was $\text{C}_{17}\text{H}_{14}\text{O}$, 2HCl , and concluded that addition occurred symmetrically on the two ethylene linkages.

Thiele and Straus⁴ showed that the equimolecular compound also existed, but gave it the chlorohydrin structure. Similarly the work of Harries⁵ led to the conclusion that α,β -unsaturated ketones behave *abnormally* with acids, addition taking place by means of the ethylene bonds and not by the carbonyl group. Stobbe,⁶ summarizing the results of these and other previous investigations, has regarded the question of structure as still unsettled.

In the present work two compounds of dibenzalacetone with trichloroacetic acid have been isolated, with the formulae $\text{C}_{17}\text{H}_{14}\text{O}$, $2\text{CCl}_3.\text{COOH}$ and $\text{C}_{17}\text{H}_{14}\text{O}$, $\text{CCl}_3.\text{COOH}$, respectively.

The equimolecular compound may be represented either as an oxonium salt or as a chlorohydrin, the carbonium structure is also possible.

¹ Claisen and Ponder, *Ann.*, **223**, 142 (1884).

² Baeyer and Villiger, *Ber.*, **34**, 2695 (1901).

³ Vorländer and Mumme, *Ibid.*, **36**, 2375 (1903).

⁴ Thiele and Straus, *Ibid.*, **36**, 2375 (1903).

⁵ Harries, *Ann.*, **330**, 185 (1904).

⁶ Stobbe, *Ibid.*, **370**, 93 (1909).

To the other compound only the oxonium or the chlorohydrin formula can be given; the former seems to be more probable. It is true that the oxonium structure here involves the assumption of hexavalent oxygen, but that such an assumption is legitimate has already been pointed out from previous results.¹ Throughout the whole of this series of investigations, however, no evidence has been obtained of "unsaturated" substances behaving abnormally in taking up more molecules of acid than "saturated" substances, *i. e.*, no addition of acid to ethylene bonds has been observed.

Summary.

The formation and stability of addition compounds of the types aldehyde—acid and ketone—acid have been investigated. From the twenty-four systems examined, eleven compounds have been isolated.

The results obtained are in complete agreement with the view, developed in previous articles, that the reaction is ionic in its nature and that the compounds formed are oxonium salts.

NICHOLS LABORATORY OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK CITY.

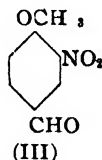
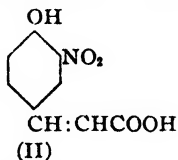
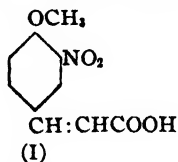
[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

3-NITRO-4-HYDROXYCINNAMIC ACID AND ITS METHYL ETHER.

By TREAT B. JOHNSON AND EDWARD F. KOHMANN.

Received October 28, 1914.

During the progress of an investigation dealing with the chemistry of nitrated protein, which is now being carried on in this laboratory, it became necessary to obtain for purposes of identification the following two acrylic acids, *viz.*, 3-nitro-4-methoxycinnamic and 3-nitro-4-hydroxycinnamic acids represented by Formulas I and II, respectively.



These two acids have already been described in the literature by Einhorn and Grabfield.² They obtained the acid (I) by application of Perkin's condensation reaction with nitro-anisic aldehyde (III), acetic anhydride and sodium acetate, and assigned to it the m. p. 140°. The corresponding hydroxyacid (II) was prepared by heating this unsaturated acid (I) in an acetic acid solution of hydrobromic acid at 100°. They assigned to this compound a m. p. of 198°.

We have now repeated this work of Einhorn and Grabfield's, and to

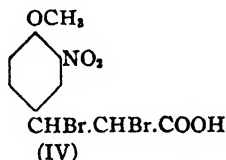
¹ Kendall and Carpenter, *Loc. cit.*

² *Ann.*, 243, 362 (1888).

our surprise have obtained two unsaturated acids having entirely different melting points than those given by these investigators. For example, by condensation of nitro-anisic aldehyde with acetic anhydride and sodium acetate, we obtained repeatedly an unsaturated acid corresponding to Formula I, which melted at $247-8^{\circ}$ instead of 140° , as observed by Einhorn and Grabfield.¹ We have also obtained this same acid from other sources,² but in no case have we obtained a lower modification melting at 140° .

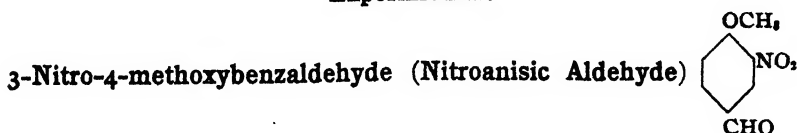
When the methoxy acid (I), melting at $247-248^{\circ}$, was heated with hydrobromic acid in acetic acid solution at 100° it easily underwent complete demethylation giving the unsaturated acid (II), melting at 223° . In this experiment also, which was conducted according to Einhorn and Grabfield's directions, we obtained no evidence of the formation of an acid melting at 198° . Both of the two acids (I) and (II) underwent esterification normally, giving their corresponding ethyl esters melting at 100° and $110-111^{\circ}$, respectively. These two compounds were apparently identical with the two esters described by Einhorn and Grabfield.¹

Our acid (I) melting at $247-248^{\circ}$ differed from Einhorn and Grabfield's acid melting at 140° , in its behavior towards bromine. They state that their acid added bromine easily in ether solution, giving the dibromo-acid (IV).



Our compound was far less reactive. In fact, no addition of halogen took place when it was subjected to the conditions of their experiment. On the other hand, it added bromine in cold, glacial acetic acid solution, giving the same dibromo-acid (IV) as was obtained by Einhorn and Grabfield. It melted at $178-9^{\circ}$. It is possible that the differences in m. p. of our acids and those obtained by Einhorn and Grabfield are to be explained by the fact that we are dealing here with a new case of stereo-isomerism. From the available data, however, we are unable to draw this conclusion. We have never obtained evidence thus far of the formation of isomeric modifications.

Experimental.



¹ *Loc. cit.*

² These observations will be described in a future paper by Mr. Kohmann (T. B. J.).

This aromatic aldehyde has been described in the literature. Einhorn and Grabfield¹ prepared it by nitrating anisic aldehyde below 0° with a calculated amount of nitric acid in presence of concentrated sulfuric acid. They found that it melted at 83.5° and established its structure by the observation that a substituted indigo² was not produced by treatment with sodium hydroxide and acetone. Wörner³ later repeated Einhorn and Grabfield's work and obtained what he supposed was a mononitro derivative melting at 72° . This product gave the same hydrazone as Einhorn and Grabfield's aldehyde melting at 83.5° . Wörner did not make an analysis of his nitro derivative and concludes his description of the compound with the following statement: "So bleibt der Widerspruch in den Beobachtungen des Schmelzpunkts von Metanitroanisaldehyd unaufgeklärt." This work was later repeated by Salway⁴ who found that the nitroaldehyde melts at the temperature given by Einhorn and Grabfield.⁵

Einhorn and Grabfield's nitroaldehyde is easily obtained if the experiment is conducted under the following conditions: First, prepare a mixture containing 300 g. of concentrated sulfuric acid and 15 g. of nitric acid (sp. gr. 1.42) and cool to -10° . While holding the temperature of the acid mixture below -10° , then add slowly through a dropping funnel 22.6 g. of anisic aldehyde and then let stand at the same temperature for one hour. On pouring this final solution into one liter of water the aldehyde will separate as a light yellow solid. The yield in one experiment was 18.5 g. and in another 21 g. The compound is easily purified by crystallization from alcohol and melts at 83° .

If the nitration is conducted at a temperature higher than 0° an entirely different result is obtained. Thirty grams of the aldehyde were nitrated with the same proportions of acids but the temperature of reaction was kept between 0° and $+3^{\circ}$. On pouring the resulting mixture into water we obtained a nitroaldehyde melting lower. It was apparently contaminated with an impurity. On repeated recrystallization from alcohol the melting point could not be raised above 73° . A mixture of this product and the pure aldehyde, melting at 83° , melted at $69-80^{\circ}$. This substance was apparently the same product as obtained by Wörner. It seems very probable, from what we were able to observe, that this lower melting substance is simply an inseparable mixture of the mononitroaldehyde (melting at 83°) and the dinitroaldehyde⁶ (melting at 86°). The analytical values obtained support this conclusion (Kjeldahl):

¹ *Ann.*, **243**, 370 (1888).

² *Baeyer, Ber.*, **15**, 2886 (1882).

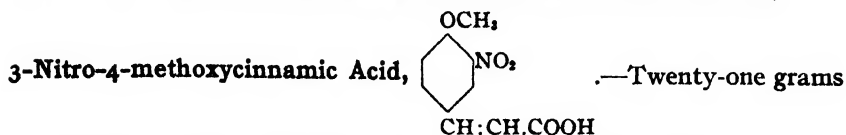
³ *Ber.*, **29**, 157 (1896).

⁴ *J. Chem. Soc.*, **95**, 1164 (1909).

⁵ *Loc. cit.*

⁶ Wörner, *Loc. cit.*

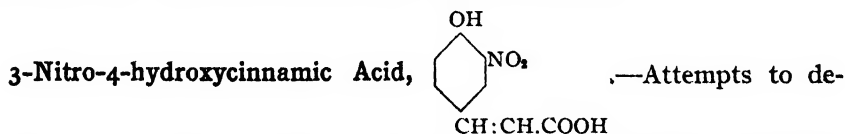
Calc. for $C_9H_7O_4N$: N, 7.73; $C_9H_7O_4N_2$: N, 12.3; found: N, 8.83, 8.87, 8.84.



of mononitro anisic aldehyde were condensed with sodium acetate (12.6 g.) and 29.4 g. of acetic anhydride by heating for 8 hrs. at $140-150^\circ$. After cooling, the resulting mixture was then triturated with dilute aqueous ammonia in order to dissolve the cinnamic acid. On acidifying the alkaline solution with hydrochloric acid the nitro compound separated in the form of yellow crystals. The acid was purified by crystallization from alcohol and separated in long, rectangular prisms or plates, which melted at $247-248^\circ$. The acid crystallized from hot water in the form of needles. It is difficultly soluble in hot water, ether and chloroform. The compound did not respond to Millon's test for a phenolic group. A careful examination of all residues and filtrates failed to reveal the presence of any other acid than this modification melting at $247-248^\circ$. Einhorn and Grabfield¹ have assigned to this compound a m. p. of 140° . The yield of purified acid was 11 g. Nitrogen determination (Kjeldahl):

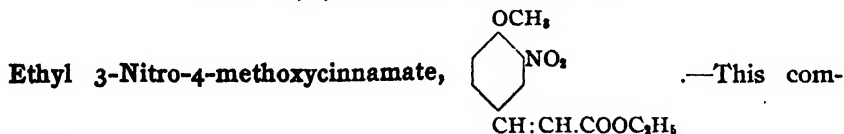
Calc. for $C_{10}H_9O_4N$: N, 6.27; found: N, 6.24.

This same acid was also obtained when the crude nitroanisic aldehyde, melting at 73° (above), was used for the condensation.



methylate the above methoxy derivative by heating with hydrochloric acid were unsuccessful. It was heated in acetic acid, saturated at 0° with hydrochloric acid gas, for 4 hrs. at 100° and at 150° for 2 hrs. without any change. Demethylation was finally effected by heating with an acetic acid solution of hydrobromic acid for 3 hrs. at 100° . After concentrating the acid solution and then pouring into water the hydroxy acid separated. This was purified for analysis by recrystallization from alcohol. It separated in the form of yellow needles which melted at 223° . Einhorn and Grabfield¹ state that this acid melts at 198° . Our product gave Millon's test for the phenolic group. Analysis (Kjeldahl):

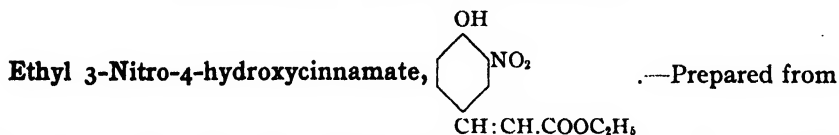
Calc. for $C_9H_7O_4N$: N, 6.70; found: N, 6.72.



¹ *Loc. cit.*

-pound was obtained by esterification of our methoxy cinnamic acid melting at 247–248°. It was obtained as a crystalline solid melting at 96–98°. It was purified for analysis by crystallization from alcohol and finally separated in large glistening prisms which melted at 99–100°. This same melting point was obtained by Einhorn and Grabfield.¹ The yield of purified ester from 1 g. of the acid was 0.7 g. Analysis (Kjeldahl):

Calc. for $C_{12}H_{13}O_4N$: N, 5.57; found: N, 5.50.



the corresponding cinnamic acid (melting at 223°) by esterification with ethyl alcohol in presence of sulfuric acid. It was purified by crystallization from alcohol and separated in yellow needles which melted at 110–111°. Einhorn and Grabfield found their ester to melt at 108.5°. Analysis (Kjeldahl):

Calc. for $C_{11}H_{11}O_4N$: N, 5.90; found: N, 5.74.

Methyl 3-Nitro-4-hydroxycinnamate.—This new ester is easily prepared by digesting the corresponding acid in methyl alcohol acidified with sulfuric acid. It crystallizes from alcohol in yellow rosetts of fine needles, which melt at 142–144°. The same ester was also obtained by heating the acid in methyl alcohol with an excess of methyl iodide and potassium hydroxide (3 molecular proportions). We obtained no evidence of the formation of methyl 3-nitro-4-methoxycinnamate under these conditions. The ester responded to Millon's test. Analysis (Kjeldahl):

Calc. for $C_{10}H_9O_4N$: N, 6.27; found: N, 6.18.



Einhorn and Grabfield¹ prepared this acid by the addition of bromine, in ether solution, to their 3-nitro-4-methoxycinnamic acid melting at 140°. They write as follows: "— so ist es auffallend, mit welcher Leichtigkeit diese Säure im Stande ist zwei Atome Brom zu fixiren." It has been our experience that our acid melting at 247° adds bromine with difficulty. Attempts to add bromine in ether solution were unsuccessful. The dibrom compound was finally obtained in the following manner: Three grams of the methoxy acid were dissolved in about 250 cc. of glacial acetic acid and the solution cooled to 40°. Two grams of bromine were then added and the solution allowed to stand for 8 days at ordinary temperature. The acetic acid was then removed by distillation in a vacuum at 50° and

¹ Loc. cit.

the addition product dissolved in alcohol and this solution evaporated to remove the alcohol. After this treatment a thick syrup was obtained. This was then dissolved in a little acetic acid and water added when we obtained 2.5 g. of a slightly gummy product, but well crystallized in the form of needles. The substance showed little tendency to crystallize from the ordinary solvents. It was finally obtained pure by dissolving in ether and then precipitating by dilution with petroleum ether. In this manner the acid was finally freed from gum and obtained in a colorless condition. It melted at $178-179^{\circ}$ as observed by Einhorn and Grabfield.¹ Analysis (Kjeldahl):

Calc. for $C_{10}H_9O_5NBr_2$: N, 3.65; found: N, 3.71.

NEW HAVEN, CONN.

ON THE BLUE HYDROCARBON OCCURRING IN SOME ESSENTIAL OILS.

[PRELIMINARY NOTE.]

BY ALFRED E. SHERNDAL.

Received November 7, 1914.

Scattered through the literature of the essential oils are frequent descriptions of blue fractions obtained in the distillation of various oils, the most intensely colored sections distilling between the temperatures, 275° and 300° , or higher. A few oils, such as those of chamomile, wormwood, and cubeb, are notable for their blue or green color before fractionation.

In a few instances where intensely colored fractions have been obtained, the investigators have thought themselves in the possession of a pure substance.² In most cases however, they have recognized that the color is due to the presence of some colored substance other than the bodies making up the bulk of the oil, and the usually accepted view has been, that this is an oxygenated substance related to the sesquiterpene alcohols.³

Semmler⁴ has summarized the literature covering these oils, and remarks that there are two views possible in regard to the blue fractions: either the greater part is colorless, and appears colored owing to the presence of a small amount of an intensely blue substance, or the sections boiling between 275° and 300° , are actually composed principally of a blue compound. That the latter is not the case, however, is evident from a survey of the literature, since the only purification method resorted to is a fractionation out of oils which contain large amounts of sesquiterpenes and sesquiterpene alcohols, with boiling points also ranging from 250°

¹ *Loc. cit.*

² Piesse, "Art of Perfumery," 1879, p. 57.

³ Bartelt, "Die Terpene und Campherarten," 1908, p. 4.

⁴ *Die Aetherischen Öle*, 3, p. 260.

to 300°. For the same reason no importance can be assigned to the various analyses of the blue fractions.

Blue products have also been obtained in the laboratory by various reactions, usually from oils composed principally of sesquiterpenes and sesquiterpene alcohols. In such cases, there seems always to have taken place a dehydration and subsequent oxidation of a sesquiterpene alcohol, or a direct oxidation of a sesquiterpene. For example, Wallach and Tuttle,¹ by the action of phosphoric anhydride, or zinc chloride on guaialol, the alcohol of guaiac-wood oil, obtained a blue sesquiterpene. They considered the color to be due to the presence of a small amount of an oxidation product. On the other hand, Gadamer and Amenomija² obtained a guaiane without blue color, by dehydrating guaialol with potassium acid sulfate.

An interesting observation was made by Hentschel and Wislicenus³ who found, on rectifying the products of the dry distillation of calcium adipate, that the fraction boiling between 135° and 145° at 30 mm., had a blue color resembling that of Roman chamomile.

Semmler and Jakubowicz⁴ obtained blue oils by heating the gurjunene sesquiterpenes in autoclaves filled with air or oxygen.

As far as the writer knows, no connection has as yet been assumed between the blue oils, and the striking color reactions which have frequently been observed when oils consisting largely of sesquiterpenes or sesquiterpene alcohols are treated in dilute solutions with mineral acids. An experiment seems, however, to indicate that such a connection may exist. If oil of gurjun balsam be dissolved in acetic anhydride, and a small amount of sulfuric acid added, the mixture becomes intensely blue, and on diluting with water and distilling the oil in a current of steam, a deep blue distillate is obtained.

Very many oils containing sesquiterpenes and related compounds, give strong color reactions when dissolved in acetic anhydride containing a trace of sulfuric acid. Of the oils examined in this laboratory, those of gurjun, amyris, and guaiac-wood give strong blue or violet colors under these conditions; santal and cedar-wood, none. This test may be used to advantage to detect adulterants in some oils, such as santal.

As to the nature of this blue constituent, nothing whatever has so far been definitely ascertained, for the reason that, as already indicated, it has not been isolated in a state of even approximate purity. A remarkable fact is that a substance with such intense color should possess a comparatively low boiling point, indicating a simple molecule. Semmler⁵ suggests the possibility of a bimolecular structure, closely related to

¹ *Ann.*, 279, 397 (1894).

² *Archiv. der pharm.*, 241, 33 (1903).

³ *Ann.*, 275, 312 (1893).

⁴ *Ber.*, 47, 2252-9 (1914).

⁵ *Aetherischen Öle*, 3, p. 266.

the sesquiterpenes, which on distillation dissociates, and on condensing, again forms a bimolecular compound, with a group similar to that in indigo: $>C : C<$. As a rule, however, the assumption has been made that the blue substance is an oxygenated compound of alcoholic nature.

The following work describes the isolation of this body in a state of purity, as shown by the analysis and reactions. As a pure substance, its remarkable properties become even more striking than before. The analysis shows it to be a highly unsaturated hydrocarbon, but the peculiar grouping of atoms to which it owes its unique properties is more difficult to speculate upon than ever.

The property which was utilized to isolate the substance, and which has heretofore not been noted, is its solubility in mineral acids of certain strengths. The method of preparation was as follows:

Fifty grams of a very blue fraction, freshly steam distilled, were shaken with 10 g. of 63% sulfuric acid, and the mixture allowed to settle over night. The acid layer was then drawn off, diluted with water, and extracted with petroleum benzine until no more blue color was taken up. The benzine solution, dark blue in color, was then shaken out with 85% phosphoric acid until no longer blue, the dark red acid solution drawn off, diluted with water, and extracted with ether. The residue from the evaporation of the ether amounted to 0.141 g., or 0.28%. This, redissolved in 50 g. of a pale yellow oil, gave a mixture with about the same tint as the original, showing that there was no appreciable loss in the preparation.

Larger quantities, isolated in this way, were further purified by distillation with steam, and finally *in vacuo*. The substance thus obtained was a slightly viscid liquid, intensely blue in thin layers, black in quantity, with a weak phenolic odor, suggesting thymol, especially when warm.

Subst., 0.2118 and 0.2294 g. gave CO_2 0.7054 and 0.7587 g.; H_2O , 0.1478 and 0.1903 g.; calc. for $C_{18}H_{18}$: C = 90.84; H = 9.15; found: C = 90.83 and 90.20; H = 9.23 and 9.28.

The molecular weight determination was made by Dr. Earl F. Farnau, of New University, by the cryoscopic method, using benzene as solvent. Found: 187.2 and 193.4 (av., 190.3); calc. for $C_{18}H_{18}$: 1.98.

The compound is, then, a hydrocarbon, having most probably the formula $C_{18}H_{18}$, and for it the writer would preserve the name "azulene," proposed in 1863 by Piesse,¹ one of the earliest investigators, for the blue fraction which he obtained from oil of worm-wood.

The specific gravity at 25° is 0.9738, when freshly steam-distilled. Exposed to light and air, it is gradually converted into a brown resin. Distilled at atmospheric pressure, the boiling point rises from 295° to 300°, leaving a tarry residue, soluble in ether with a brown color. At about 25 mm. azulene distils from 185° to 195°, leaving a brown residue of about 5%. Since the product had been previously distilled with steam, this

¹ *Compt. rend.*, 57, 1016 (1864).

shows that it cannot be distilled without change under these conditions. When evaporated on the water-bath in an open dish, a brown resin, amounting to 10%, or more, remains.

Azulene is readily soluble in most organic solvents. In 95% alcohol it is miscible in all proportions; in more dilute alcohol the solubility is much less, but even 50% alcohol takes up enough to be tinted, a decided blue.

Its solubility in strong inorganic acids, which makes its isolation possible, is especially remarkable. In 60 to 65% sulfuric acid, azulene dissolves to a clear yellow, strongly fluorescent solution; on dilution with water, it is thrown out again as a blue oil, apparently unchanged. It also dissolves in 50% sulfuric acid, but less readily. The solution in phosphoric acid is remarkable for its fluorescence; reddish yellow by transmitted light, intense apple green by reflected light. These acid solutions can be extracted with benzine without removing any azulene, and by repeating several times, a product can be obtained, free from sesquiterpenes or alcohols.

Azulene is strongly resistant to the action of even strong sulfuric acid. When heated with two parts of 94% acid for fifteen hours on the water-bath, a dark brown solution results, which, on diluting with water, again yields the blue oil. Strong formic acid dissolves it with a green color, but in acetic acid the color remains unchanged, as in the neutral solvents. On mixing dry ether solutions of azulene and hydrochloric acid, no change in color was observed.

Nitric acid in acetic acid solution produces yellow amorphous substances, not further examined.

The oxidation of azulene with permanganate has so far yielded only lower fatty acids.

It is not attacked by sodium in hot alcohol, nor does heating with strong alkali affect the color.

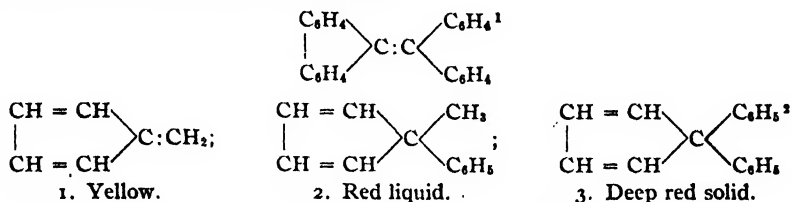
By the action of acetic anhydride and sulfuric acid, a substance was obtained, evidently a sulfonic derivative, which was soluble in water. On adding sodium carbonate in excess a sodium salt separated out, which was recrystallized from hot water. The water solution of the salt is colored violet, and changes to a light green on acidifying. If then shaken with ether, the latter becomes violet, and this color is again taken out by shaking with alkali.

The sodium salt, on heating, gives off blue fumes which condense to a blue oil; at the same time sulfur dioxide is liberated.

On standing three months in a corked bottle, a preparation of the sodium salt had decomposed into a mixture of oil and resin.

The water solution gives blue precipitates with barium and calcium solutions, and is decolorized by bromine water.

It appears established that azulene is closely related to the sesquiterpenes. From no other class of compounds have hydrocarbons been obtained which show such intense color. Colored hydrocarbons which have so far been prepared, are characterized by complex structure or a dense arrangement of the atoms, the intensity of the color increasing with the size of the molecule; for example:



Rubicen, a red hydrocarbon, $\text{C}_{26}\text{H}_{14}$, m. p. 306° .³

It is obvious that in azulene we have an entirely different and unique chemical compound. We hope, in a subsequent communication, to collect further data on this interesting substance.

The writer wishes here to acknowledge his indebtedness to Dr. Francis D. Dodge for helpful suggestions as well as for aid in obtaining material used in connection with the above work.

LABORATORY OF THE DODGE AND OLCOTT CO.,
BAYONNE, N. J.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]
RESEARCHES ON HYDANTOINS. XXIX. GEOMETRICAL ISOMERISM IN THE HYDANTOIN SERIES.

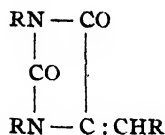
By THOMAS B. JOHNSON AND SIDNEY E. HADLEY.
Received November 19, 1914.

In order that geometrical isomerism may be shown in an unsaturated carbon compound, two fundamental conditions must be fulfilled: first, that the molecule contains a double bond between two of its carbon atoms, and second, that the two radicals linked to each of these two carbon atoms must be different. Theoretically, the accepted structural formula of an *aldehyde-hydantoin* condensation product (I) fulfills both these conditions and consequently a hydantoin of this type might be expected to occur in *cis*- and *trans*-modifications. The constitutions of such isomeric forms might be expressed by the two graphic Formulas II and III, respectively. Several unsaturated compounds of this type (I) have been prepared in this laboratory, but hitherto we have not detected the occurrence of more than one modification. In this paper we will now discuss the first case of this type of isomerism so far observed in the hydantoin series.

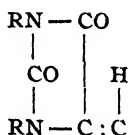
¹ Graebe, *Ber.*, **26**, 2334 (1892); **25**, 3146 (1891).

² Thiele, *Ber.*, **33**, 668, 851, 3395 (1900); *Ibid.*, **36**, 842 (1903); *Ann.*, **319**, 226 (1901).

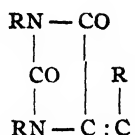
³ Pummerer, *Ber.*, **45**, 294 (1912).



(I)

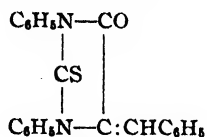


(II)

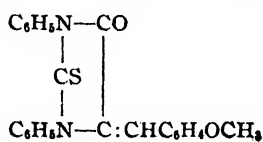


(III)

1,3-Diphenyl-2-thiohydantoin (VI), which was first synthesized in this laboratory by Wheeler and Brautlecht,¹ condenses with benzaldehyde and anisic aldehyde forming the corresponding condensation products represented by Formulas IV and V, respectively. The benzal com-



(IV)



(V)

pound (IV), which is the only one of the two hydantoin of any interest in this investigation, was found by Wheeler and Brautlecht to melt at 194°. Having occasion to prepare this hydantoin we found, to our surprise, on repeating this experiment, that the hydantoin (m. p. 194°) described by Wheeler and Brautlecht² is not the only product of this reaction. In fact we were able to isolate an isomeric product which melted several degrees lower than Wheeler and Brautlecht's hydantoin. This modification, however, was formed in such small quantities and possessed such unfavorable properties that we were unable to establish conclusively its constitution by chemical means. The structure of the modification melting at 197° was proved by the fact that it underwent reduction with hydriodic acid giving the hydantoin (IX) previously described by Johnson and Shepard.³

Notwithstanding the fact that the hydantoin (IV), melting at 197°, is a stable and definite compound, it undergoes a remarkable change when it is desulfurized by digestion with chloroacetic acid. It combines with this halogen acid, giving apparently an addition product, which can easily be broken down by acid hydrolysis forming smoothly two well defined isomeric hydantoin. We have now concluded that these are geometrical isomers of 1,3-diphenyl-4-benzalhydantoin whose structures may be represented by Formulas VII and VIII. They melt at 192° and 152°, respectively. The higher melting modification, which we have represented as the *trans*-form, is the chief product of the reaction. The lower melting form, or *cis*-modification, is not formed in large amount

¹ *Am. Chem. Jour.*, 45, 446 (1911).

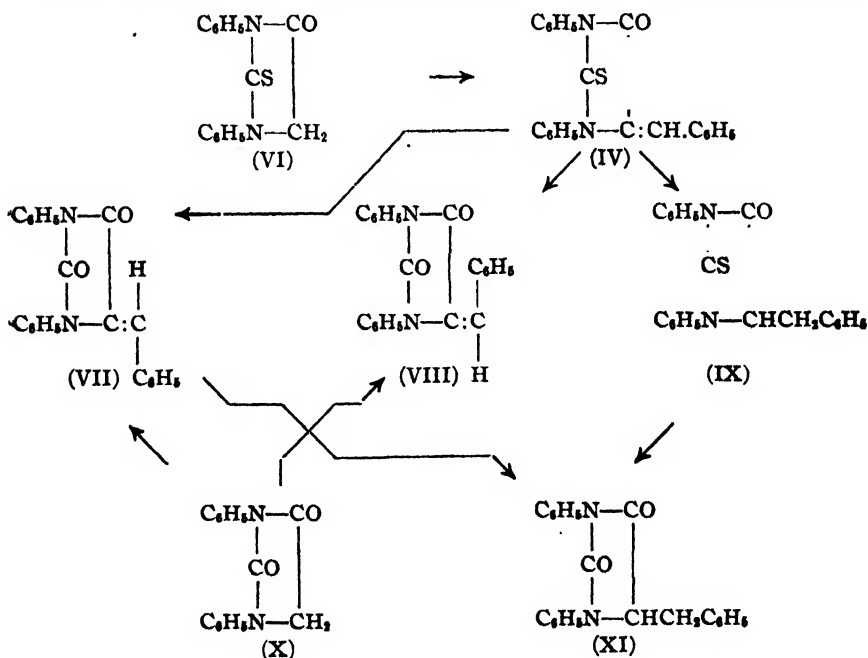
² The true melting point of this hydantoin is 197°.

³ *THIS JOURNAL*, 36, 1735 (1914).

and is characterized by its greater solubility. That this interesting case of hydantoin isomerism is to be explained by the presence of the double bond in the unsaturated molecule is established by the fact that both modifications (VII and VIII) undergo reduction smoothly with hydriodic acid, giving the same saturated compound—1,3-diphenyl-4-benzylhydantoin represented by Formula XI. This hydantoin has previously been described by Johnson and Shepard.¹

We have now made the interesting observation that these same two isomeric modifications of 1,3-diphenyl-4-benzalhydantoin are also formed by condensation of 1,3-diphenylhydantoin² (X) with benzaldehyde. Wheeler and Hoffmann³ state that this hydantoin does not condense with anisic aldehyde when heated with it in the presence of sodium acetate, acetic acid and acetic anhydride. With benzaldehyde the condensation can easily be brought about with smooth formation of hydantoin. The *trans*-modification, however, is the chief product of the reaction. Both forms were isolated and their identity with the two hydantoin obtained by desulfurization of 1,3-diphenyl-4-benzalthiohydantoin completely established.

These various transformations are expressed by the following formulas:



¹ *Loc. cit.*

² Bischoff and Häusdörfer, *Ber.*, 25, 2274 (1892).

³ *Am. Chem. J.*, 45, 368 (1911).

Experimental Part.

1,3-Diphenylthiohydantoin (VI).—This hydantoin, which served as the starting point in our investigation, was prepared according to the directions of Wheeler and Brautlecht¹ by heating ethyl anilinoacetate with phenylisothiocyanate. While this compound is easily obtained in quantity by this method, we have observed, however, that it is not the only product of the reaction. In several cases we have obtained a secondary product which melts several degrees higher than the diphenylthiohydantoin (212°). Whether we are dealing here with an unique case of isomerism or polymerization will be decided by a further investigation.

1,3-Diphenylhydantoin (X).—This hydantoin² is easily obtained by desulfurization of 1,3-diphenylthiohydantoin. This was accomplished by digestion of the thiohydantoin with chloroacetic acid. Fifteen grams of the thiohydantoin and 150 g. of chloroacetic acid were digested with 50 cc. of water, on a sand bath, for 9 hrs. The mixture was then diluted with water, when a gummy product was obtained. This was separated from the water solution and finally heated with boiling hydrochloric acid when thioglycollic acid and diphenylhydantoin were formed. The latter was purified by recrystallization from alcohol and melted at 139°. The yield of purified material was 10.5 g.

1,3-Diphenyl-4-benzal-2-thiohydantoin (IV).—Wheeler and Brautlecht¹ first prepared this compound by condensing benzaldehyde with 1,3-diphenylthiohydantoin and found it to melt at 194°. We now find on repeating this experiment that this hydantoin is not the only product of this reaction. While this hydantoin, which we found to melt at 197°, is the chief product formed we have observed that it is accompanied by two other substances of characteristic properties. One of these is apparently a stereoisomeric modification of the hydantoin (melting at 197°) and the other is apparently identical with the substance of unknown constitution, which is formed by heating phenylisothiocyanate with ethyl-anilinoacetate.

The condensations were generally carried out in the following manner: Forty-seven grams of the diphenylthiohydantoin, 40 g. of benzaldehyde and 76 g. of anhydrous sodium acetate are dissolved in 245 cc. of hot glacial acetic acid and the solution heated in an oil bath at 150° for 12–14 hrs. The acid solution is then diluted copiously with cold water and cooled, when the crude hydantoin separates in a granular condition. The yield of crude material varies somewhat but generally is between 90–98% of the theoretical. On digesting this crude product with glacial acetic acid, all dissolves with the exception of a small amount of yellow material which generally melts above 280°. On cooling the acetic acid solution

¹ *Loc. cit.*

² Bischoff and Häusdörfer, *Loc. cit.*

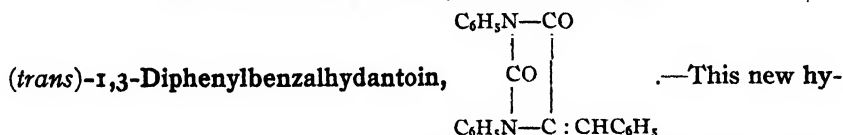
the diphenylbenzalhydantoin separates at once and is easily obtained in a pure condition (m. p. 197°) by recrystallization from acetic acid. After separation of the diphenylbenzalhydantoin a dark red acetic acid filtrate is always obtained, which contains apparently a small amount of a substance isomeric with the hydantoin melting at 197° . This can be isolated in an impure condition by evaporating the acetic acid filtrate at 100° to remove acetic acid and then triturating the gummy residue with hot alcohol. The coloring material and isomer are removed by this treatment, leaving behind the 1,3-diphenyl-4-benzalthiohydantoin. On cooling the alcoholic solution the isomer separates as a red powder having no definite melting or decomposition point. It was not present in large amount. A nitrogen determination gave (Kjeldahl):

Calc. for $C_{22}H_{16}ON_2S$: N = 7.8; found: N = 7.36.

In another experiment when we used 10 g. of the thiohydantoin, 15 g. of sodium acetate, 11 g. of benzaldehyde and 50 cc. of glacial acetic acid, we obtained 13 g. of the hydantoin melting at $196-197^{\circ}$. This yield was nearly the theoretical amount.

1,3-Diphenyl-4-benzyl-2-thiohydantoin (IX).—This hydantoin has been described in a previous paper by Johnson and Shepard.¹ We now find that the same compound is also formed by reduction of the above benzalthiohydantoin with hydriodic acid in the presence of phosphorus. This was accomplished by digesting the hydantoin with the halogen acid and phosphorus in acetic acid solution. The hydantoin was purified by crystallization from alcohol. It separated in rosetts of needles which melted at 130° . Analysis (Kjeldahl):

Calc. for $C_{22}H_{18}ON_2S$: N = 7.8; found: N = 7.53.



dantoin is easily obtained by desulfurization of the corresponding 2-thiohydantoin. Three grams of the thiohydantoin (melting at 197°) and 30 g. of chloroacetic acid were digested for 2 hrs. A clear solution was obtained. This was then diluted with water when a light yellow, gummy product separated. After separation from the water this substance was then boiled with strong hydrochloric acid when it was completely changed into the above hydantoin. The yield of crude material was 2.7 g. The hydantoin was purified by crystallization from glacial acetic acid. It separated from this solvent, on cooling, in light yellow prisms with tetrahedral form and melted at 192° . They did not respond to a test for sulfur. Nitrogen determination (Kjeldahl):

Calc. for $C_{22}H_{18}O_2N_2$: N = 8.22; found: N = 8.39, 8.11.

¹ *Loc. cit.*

(*cis*)-1,3-Diphenylbenzalhydantoin.—In another experiment we used the following proportions: 14 g. of diphenylbenzalthiohydantoin, 140 g. of chloroacetic acid and 47 cc. of water. These were heated for 5 hrs. when a similar result was obtained as in the previous experiment. The gummy product was decomposed in the usual manner by digesting with hydrochloric acid and the resulting crude hydantoin then purified by crystallization from acetic acid. The hydantoin melting at 192° was obtained as before. After separation of this substance the acetic acid filtrate was then concentrated and cooled, when we obtained a crystalline substance which melted at $145\text{--}152^{\circ}$. This was identified as an *isomer* of 1,3-diphenyl-4-benzalhydantoin. It was purified by crystallization from glacial acetic acid and separated in rosets of prisms which melted sharply at $150\text{--}152^{\circ}$. It did not rearrange into the *trans*-modification when heated at 192° . The yield of purified material was 1 g. Analysis (Kjeldahl):

Calc. for $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$: N = 8.22; found: N = 8.03.

In a third experiment we obtained, after desulfurization of 15 g. of 1,3-diphenyl-4-benzal-2-thiohydantoin, 10.5 g. of the *trans*-hydantoin melting at 192° and 1.5 g. of the *cis*-modification melting at 152° .

The Condensation of Benzaldehyde with 1,3-Diphenylhydantoin.—1,3-Diphenylhydantoin undergoes condensation with benzaldehyde giving *cis*- and *trans*-1,3-diphenyl-4-benzalhydantoins. The yield, however, of the *cis*-modification is very small. In our first experiment the condensation was effected by digesting 5 g. of the diphenylhydantoin and 3 g. of benzaldehyde with 15 g. of sodium acetate, 10 cc. of acetic anhydride and 20 cc. of glacial acetic acid for 4 hrs. at 150° . On cooling the resulting solution and then diluting with water the hydantoin separated. This was purified by recrystallization from acetic acid and melted at 192° . This same result was also obtained when the condensation was effected in the presence of potassium acetate. In neither of these experiments did we detect the presence of any *cis*-diphenyl-4-benzalhydantoin melting at 152° . It was only by working with larger quantities of material that we were finally able to isolate the *cis*-modification. In a third experiment 47 g. of the diphenylhydantoin were condensed with benzaldehyde according to the described conditions. After pouring the reaction mixture into water, to separate the crude hydantoin, and then crystallizing from acetic acid, we obtained 28 g. of the *trans*-hydantoin, melting at 192° . The acetic acid filtrates were then combined and evaporated at 100° to remove the excess of acetic acid when we obtained a dark red, gummy residue. This product was triturated with warm 95% alcohol and the mixture allowed to stand for several hours, when we finally obtained about 5–6 g. of a semisolid substance insoluble in the alcohol. This was separated from adhering oil by filtering and purified by recrystallization from acetic

acid. After the first crystallization this melted at 130–150°, indicating a mixture of the two isomeric hydantoins. Separation was finally effected by fractional crystallization from acetic acid. The *cis*-modification is more soluble in this solvent than the *trans*-form and in this case sufficient material was available to enable us to isolate the *cis*-modification. It crystallized from acetic acid in needles which melted at the same temperature as the hydantoin obtained by desulfurization of the corresponding 2-thiohydantoin. A mixture of the two substances melted at 150–2°.

Reduction of *cis*- and *trans*-1,3-Diphenyl-4-benzalhydantoin.

1,3-Diphenyl-4-benzylhydantoin (XI).—This hydantoin, which has been described in a previous paper by Johnson and Shepard,¹ is formed when the *cis*- and *trans*-modifications of 1,3-diphenyl-4-benzalhydantoin are reduced with hydriodic acid. This was accomplished by digesting the unsaturated hydantoins in glacial acetic acid with hydriodic acid and in presence of a little red phosphorus. After the reduction was complete the solution was then diluted with water when the hydantoin separated as a gum. In some experiments the excess of acetic acid was first removed by evaporation at 100°, but under both conditions the same gum was obtained. This was purified by dissolving in ether, washing with a little bisulfite solution to remove a trace of iodine and then drying the ether solution over anhydrous calcium chloride. On allowing the ether to evaporate the hydantoin was finally obtained in a crystalline condition melting at 58–62°. The compound is very hygroscopic. It is extremely soluble in cold alcohol, ether, benzene, acetic acid, acetone, chloroform, ethylacetate and ligroin but practically insoluble in water. It does not dissolve in cold sodium hydroxide solution. The compound agreed in all its properties with Johnson and Shepard's 1,3-diphenyl-4-benzylhydantoin.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON PYRIMIDINES. LXXIII. ALKYLATION OF 2-MERCAPTOPYRIMIDINES.

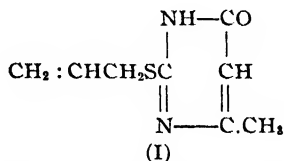
BY TRENT B. JOHNSON AND HOWARD W. HAGGARD.

Received November 23, 1914.

The papers so far published from this laboratory on the alkylation of 2-mercapto-6-oxypyrimidines have been confined to a description of results obtained from the study of mercapto compounds in which the mercapto grouping contained a saturated alkyl radical, *viz.*, CH₃-, C₂H₅-, C₆H₅CH₂-, etc. In all of the cases examined, with one exception, mercapto groups of this type have favored substitution in the 1- and 3-positions of the pyrimidine ring. With these results at hand it then became

¹ *Loc. cit.*

of interest to determine what influence, if any, negative mercapto groupings would have on the formation of alkylation products. In other words, would such combinations be favorable to select for the preparation of 3-alkyl derivatives? In order to acquire further data on this interesting question¹ we selected for study a mercaptopyrimidine containing an unsaturated allyl group in the 2-position, *viz.*, 2-allylmercapto-4-methyl-6-oxypyrimidine (I). The results of this investigation are now presented in this paper.



2-Allylmercapto-4-methyl-6-oxypyrimidine (I) was prepared by the action of allylbromide or iodide on the sodium salt of 2-thio-4-methyluracil (V). At the beginning of our work we first compared the behavior of this new mercaptopyrimidine (I) with that of 2-methylmercapto-4-methyl-6-oxypyrimidine (II)² towards methyl iodide and allylbromide, respectively, in order to find out whether both reactions would lead to the formation of isomeric nitrogen-substitution products. To our surprise they underwent alkylation in an entirely different manner. The sodium salt of the allylmercapto-4-methyl-6-oxypyrimidine (I) interacted with methyl iodide giving smoothly 2-allylmercapto-1,4-dimethyl-6-oxypyrimidine represented by Formula VIII. We obtained no evidence of the formation of a 3-methylated derivative. On the other hand, the sodium salt of 2-methylmercapto-4-methyl-6-oxypyrimidine (II) interacted smoothly with allylbromide forming an oxygen derivative, or the inido ester combination, *viz.*, 2-methylmercapto-4-methyl-6-allyloxy-4,5-dihydropyrimidin-2-one corresponding to Formula III. This latter result is of especial interest and is not in accord with our previous observations. Alkylations with saturated primary halides have led to the formation of nitrogen substituted pyrimidines. The allyl group apparently has a greater affinity for the oxygen of the NH-CO grouping than for the nitrogen.

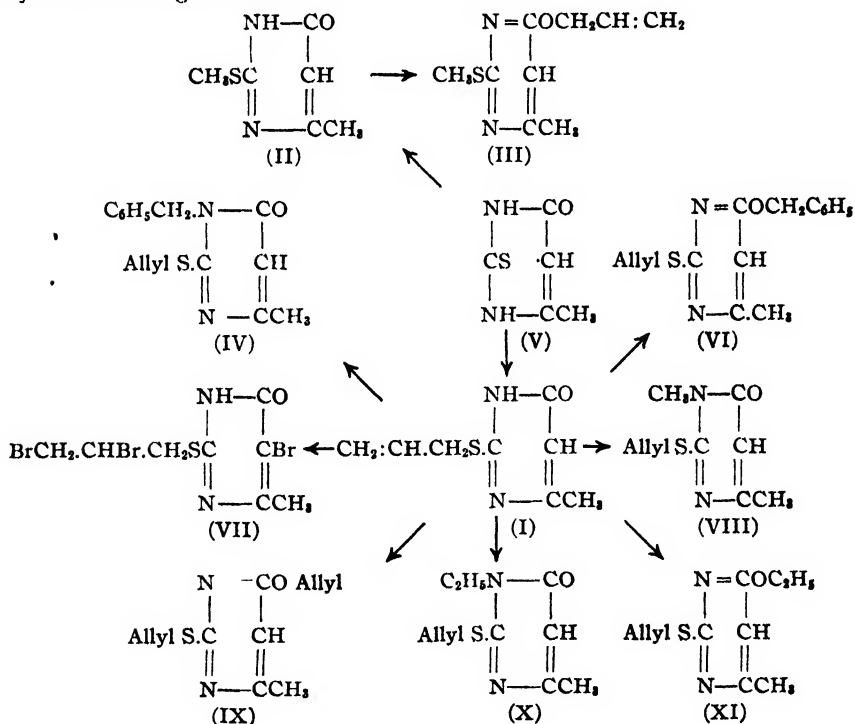
While methyl iodide interacted with the sodium salt of 2-allylmercapto-4-methyl-6-oxypyrimidine (I), giving normally a 1-methyl derivative (VIII), on the other hand, when we applied a similar reaction with allylbromide, ethylbromide and benzylchloride abnormal results were obtained. *In no case did we observe the formation of 3-substitution products.* Allylbromide interacted with the sodium salt of the pyrimidine (I) giving exclusively an oxygen derivative corresponding to Formula IX. This

¹ This question is of special biochemical interest to us because of its connection with our synthetical work, now in progress, on pyrimidine nucleosides (T. B. Johnson).

² Wheeler and Merriam, *Am. Chem. J.*, **29**, 486 (1903).

result is perfectly analogous to that obtained by the action of the unsaturated halide (allylbromide) on the sodium salt of 2-methylmercapto-4-methyl-6-oxypyrimidine (II).

Benzylchloride and ethylbromide both reacted with the sodium salt of the allylpyrimidine (I) in an analogous manner giving mixtures of their corresponding oxygen derivatives (VI) and (XI) and 1-substituted pyrimidines represented by Formulas IV and X, respectively. The structures of these various mercaptopyrimidines were established by their behavior on acid hydrolysis. A description of the properties of these various compounds and their chemical behavior is given in the experimental part of this paper. When 2-allylmercapto-4-methyl-6-oxypyrimidine (I) was allowed to interact with bromine it was converted into the saturated pyrimidine (VII). The various changes discussed above are represented by the following formulas:



Experimental.

2-Allylmercapto-4-methyl-6-oxypyrimidine (I).—This mercaptopyrimidine was prepared by digesting the sodium salt of 2-thio-4-methyluracil¹ in alcohol, with the calculated amount of allylbromide. After the reaction was complete the solution was filtered from sodium bromide

¹ List, *Ann.*, **236**, 3 (1886).

and the alcohol then evaporated. The pyrimidine was obtained in a crystalline condition and was purified by recrystallization from hot water. It separated from this solvent, on cooling, in colorless needles which melted at 131° to a clear oil without decomposition. The pyrimidine is very soluble in alcohol. From 25 g. of 2-thio-4-methyl-6-oxypyrimidine we obtained 30 g. of the mercaptopyrimidine. Nitrogen determination (Kjeldahl):

Calc. for $C_8H_{10}ON_2S$: N = 15.4; found: 15.5 and 15.6.

1-Methyl-2-allylmercapto-4-methyl-6-oxypyrimidine (VIII).—One and five-tenths grams of sodium were dissolved in 75 cc. of absolute alcohol and 10 g. of the preceding 2-allylmercaptopyrimidine dissolved in the solution. An excess of methyl iodide was then added and the mixture digested until neutral to turmeric and litmus. The alcohol was then removed by heating under diminished pressure, when we obtained the methylpyrimidine mixed with sodium iodide. This residue was then triturated with water to dissolve the iodide and the pyrimidine extracted with ether. Calcium chloride formed an insoluble addition-product with this pyrimidine and consequently we were obliged to dry its ether solution over anhydrous potassium carbonate. After complete drying, the ether was then allowed to evaporate in the air, when we obtained the pyrimidine in the form of hexagonal tables melting at 43° to an oil. It is very soluble in ligroin, ethyl acetate, chloroform and benzene. Nitrogen determination (Kjeldahl):

Calc. for $C_9H_{12}ON_2S$: N = 14.3; found: N = 14.4.

Hydrolysis with Hydrochloric Acid.—Four grams of the mercaptopyrimidine were dissolved in an excess of hydrochloric acid and the solution boiled for several hours to remove the mercapto group. On evaporating to dryness we obtained 1,4-dimethyluracil¹ which melted at 256° without further purification. This pyrimidine contained a small amount of impurity which was not removed by crystallization from alcohol or water. A mixture of this substance and some 1,4-dimethyluracil (m. 258°) melted at $256-7^{\circ}$. Nitrogen determination (Kjeldahl):

Calc. for $C_6H_8O_2N_2$: N = 20.00; found: N = 20.3.

2-Allylmercapto-4-methyl-6-alloxyprymidine (IX).—This pyrimidine was formed by digesting the sodium salt of 2-allylmercapto-4-methyl-6-oxypyrimidine, in alcohol, with the calculated amount of allylbromide. After the reaction was complete the alcohol was then removed by heating under diminished pressure and the pyrimidine finally dissolved in ether and the solution dried over potassium carbonate. On evaporating the ether the pyrimidine was obtained as an oil, which showed no signs of crystallizing on long standing. No attempt was made to distil this oil but it was digested for several hours with concentrated hydrochloric acid.

¹ Behrend and Dietrich, *Ann.*, 309, 268 (1899).

Allylmercaptan was formed and after evaporation of the acid, 4-methyluracil was the only pyrimidine identified. This was purified by crystallization from hot water and did not melt below 290° . Nitrogen determination (Kjeldahl):

Calc. for $C_5H_6O_2N_2$: N = 22.22; found: N = 21.95 and 22.1.

Action of Bromine on 2-Allylmercapto-4-methyl-6-oxypyrimidine: 2-Dibromopropylmercapto-4-methyl-5-bromo-6-oxypyrimidine (VII).—This pyrimidine is formed smoothly by dissolving 2-allylmercapto-4-methyl-6-oxypyrimidine in glacial acetic acid and then adding the required amount of bromine (2 molecular proportions). The bromine was introduced by passing air through the liquid bromine and then conducting the same into the acetic acid solution. The reaction was instantaneous. After allowing to stand for 2 or 3 days the tribromopyrimidine finally deposited. The yield was about 87% of the theoretical. It was purified by crystallization from boiling 95% alcohol and separated as rosetts of needles, which melted at 160 – 165° with decomposition. Nitrogen determination (Kjeldahl):

Calc. for $C_8H_8N_2Br_3S$: N = 6.65; found: N = 6.9.

The Action of Ethylbromide on 2-Allylmercapto-4-methyl-6-oxypyrimidine.—By the action of ethylbromide on the sodium salt of this mercaptopyrimidine we obtained an inseparable mixture of 1-ethyl-2-allylmercapto-4-methyl-6-oxypyrimidine and 2-allylmercapto-4-methyl-6-ethoxypyrimidine. Two and two-tenths grams of sodium were dissolved in absolute alcohol and 15 g. of the allylmercaptopyrimidine dissolved in the solution. Ten and five-tenths grams of ethylbromide were then added and the solution warmed on the steambath until the reaction was complete. The sodium bromide was separated by filtration and the alcohol evaporated under diminished pressure, when we obtained an oil, which refused to solidify when cooled to 0° . It was dissolved in ether, dried over potassium carbonate and finally distilled under diminished pressure. We obtained 10 g. of the mixed pyrimidines boiling from 168 – 175° at 14–18 mm. This oil showed no signs of crystallizing, and a nitrogen determination (Kjeldahl) agreed with the calculated value for an ethyl derivative (13.2%). The oil was insoluble in sodium hydroxide solution. In order to determine the constitution of the ethylpyrimidines, the oil was suspended in an excess of strong hydrochloric acid, digested for 17–18 hrs. and the solution then evaporated to dryness. We obtained a mixture of 4-methyluracil and 1-ethyl-4-methyluracil. They were separated by trituration of the crude mixture with an excess of cold chloroform when the ethylpyrimidine dissolved. The insoluble material did not melt below 290° , was free from sulfur and agreed in all its properties with 4-methyluracil. The chloroform solution was evaporated to dryness and the residue of ethylmethyluracil purified by crystallization from hot water. It separated in color-

less prisms, which melted at 193–195°. ¹ The weight of purified methyluracil was 3.2 g. and of ethylmethyluracil 3.0 g. Therefore, the original oil was a mixture of approximately equal parts of 1-ethyl-2-allylmercapto-4-methyl-6-oxypyrimidine (X) and 2-allylmercapto-4-methyl-6-ethoxypyrimidine (XI).

The Action of Benzylchloride on 2-Allylmercapto-4-methyl-6-oxypyrimidine.—Benzylchloride reacted with the sodium salt of this mercaptopyrimidine to form two pyrimidines, *viz.*, 1-benzyl-2-allylmercapto-4-methyl-6-oxypyrimidine and 2-allylmercapto-4-methyl-6-benzoxypyrimidine. The operation was conducted as described in the preceding experiment and the following proportions were used, *viz.*, 1.5 g. of sodium, 10 g. of the allylmercaptopyrimidine, 6 g. of benzylchloride and 75 cc. of absolute alcohol. After filtration from sodium chloride and removal of the alcohol under diminished pressure we obtained the mercaptopyrimidines in the form of a thick oil, which did not solidify on cooling. After drying in ether solution over potassium carbonate the oil was purified by distillation. It practically all boiled at 225–235° at 14–15 mm. and a nitrogen determination (Kjeldahl) agreed with the calculated value for a monobenzyl derivative.

Calc. for $C_{16}H_{16}ON_2S$: N = 10.3; found: N = 10.5.

In order to determine the composition of this mixture the oil was digested with concentrated hydrochloric acid until completely hydrolyzed and the acid solution then evaporated to dryness. A mixture of 4-methyluracil and 1-benzyl-4-methyluracil² was obtained. They were separated from each other by a fractional crystallization from water. The benzylpyrimidine was obtained in colorless prisms, which melted at 194–5°, and a mixture of this with some 1-benzyl-4-methyluracil prepared by Wheeler and McFarland³ melted at exactly the same temperature. Methyluracil was isolated in a pure condition from the aqueous filtrates and did not melt below 300°. We obtained no evidence of the presence of 3-benzyl-4-methyluracil.⁴ The weights of methyluracil and the benzylpyrimidine were about equal. Therefore, the product of the alkylation was a mixture of two pyrimidines, *viz.*, 2-allylmercapto-4-methyl-6-benzoxypyrimidine (VI) and 1-benzyl-2-allylmercapto-4-methyl-6-oxypyrimidine (IV).

Action of Allylbromide on the Sodium Salt of 2-methylmercapto-4-methyl-6-oxypyrimidine. 2-Methylmercapto-4-methyl-6-alloxyprymidine (III).—The 2-methylmercapto-4-methyl-6-oxypyrimidine used in our work was prepared by alkylation of 2-thio-4-methyluracil with methyl iodide in alcoholic solution and in presence of the required amount of

¹ Hoffmann, *Ann.*, 253, 68 (1889); Hagen, *Ibid.*, 244, 8 (1888).

² Wheeler and McFarland, *Am. Chem. J.*, 42, 101 (1909).

³ *Loc. cit.*

⁴ Wheeler and McFarland, *Loc. cit.*

sodium ethylate. For the alkylation, the following proportions were used, *viz.*, 15 g. of the 2-mercaptopyrimidine, 2.4 g. of sodium, 14 g. of allylbromide and 75-100 cc. of absolute alcohol. After the reaction was complete the sodium bromide was filtered off and the excess of alcohol removed in the usual manner, when we obtained the allyl derivative as a yellow oil. This was extracted with ether dried over potassium carbonate and then further purified by distillation under diminished pressure. It practically all boiled at 160-164° at 17 mm. A nitrogen determination (Kjeldahl) gave:

Calc. for $C_9H_{12}ON_2S$: N = 14.2; found: N = 14.3.

The constitution of this mercaptopyrimidine was established by its behavior on hydrolysis. It was converted smoothly into 4-methyluracil by digestion with hydrochloric acid. This was purified by crystallization from hot water and did not melt or decompose below 300°. Analysis (Kjeldahl):

Calc. for $C_6H_8O_2N_2$: N = 22.2; found: N = 22.2.

NEW HAVEN, CONN.

ON 1-PHENYL-4,5-DIHYDRO-5-OXY-3-TRIAZOLYLSULFINIC ACID AND 1-PHENYL-4,5-DIHYDRO-5-OXY-3-TRIAZOLYLMETHYLSULFONE.

[EIGHTEENTH¹ COMMUNICATION ON URAZOLES.]

By E. W. ESSLINGER AND S. F. ACRER.

Received November 14, 1914.

In developing the study of tautomerism as illustrated in the urazoles, it has been found² that 1-phenyl-3-thiourazole (I) apparently gives only one mono-alkyl derivative (II) when treated with an alkyl halide, diazomethane or alcoholic hydrochloric acid, or when its salts are treated with an alkyl halide or sulfate. It will be recalled that the corresponding 3-oxyurazole always yields a mixture of the 2-N-ester (V) and 3-O-ester (VI) under these conditions, the yields varying widely with the different salts and alkyl halides used. A mathematical development of our theory³ showed that the facts can be interpreted consistently on the idea that the salts of the 3,5-dioxyurazoles exist in two tautomeric⁴ forms (III) and (IV),

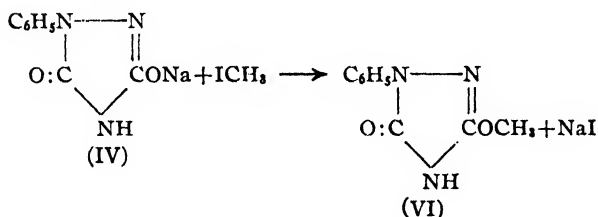
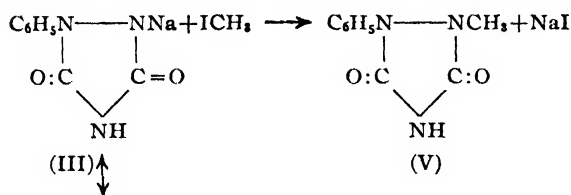
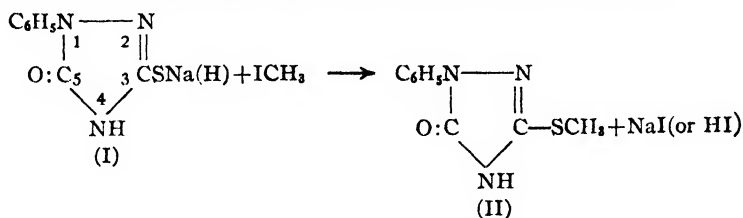
¹ This work was presented in June, 1912, by E. W. Esslinger as a partial fulfillment of the requirements for the degree of Master of Arts in the Johns Hopkins University. For previous work see *Ber.*, 33, 1530 (1900); 35, 553 (1902); 36, 3139 (1903); 37, 184, 618 (1904); 41, 3199 (1908); *Science*, 30, 617 (1909); *Am. Chem. J.*, 27, 118 (1902); 31, 185 (1904); 32, 606 (1904); 37, 71, 361 (1907); 38, 1 (1907); 39, 124, 226 (1908); 43, 358 (1910); 44, 219 (1910); 49, 116 (1913). [We are indebted to the Carnegie Institution of Washington for aid in these researches.]

² *Ber.*, 36, 3152 (1903).

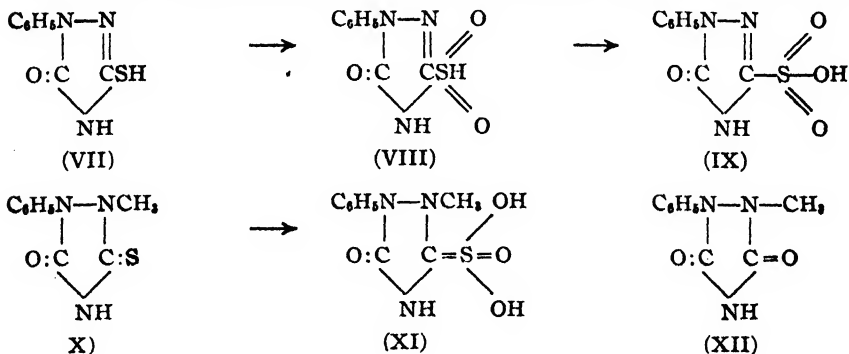
³ *Ibid.*, 41, 3199 (1908); *Am. Chem. J.*, 43, 505 (1910).

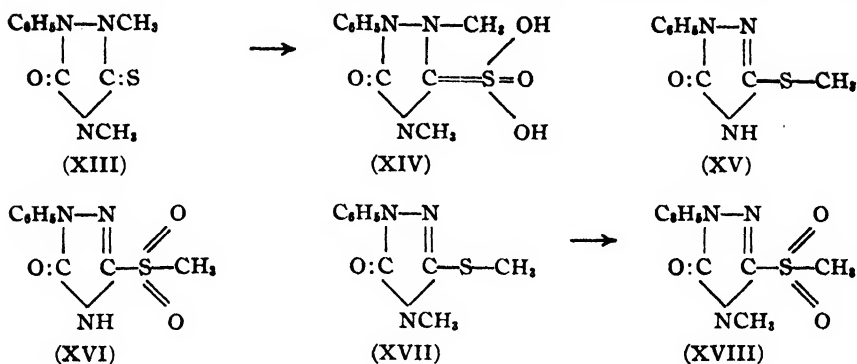
⁴ *Ibid.*, 37, 70 (1907); 38, 1 (1907); 43, 505 (1910); 44, 219 (1910); 49, 116 (1913).

whose molecules and anions are in equilibrium and react with the molecular alkyl halide to give the esters (V) and (VI). Since 1-phenyl-3-thiourazole (I) yields only one ester (II), it seemed probable that very little of the tautomeric form corresponding to (III) enters into the reaction.



On account of the difficulties involved and the expense of the necessary materials the 2-N-esters (X) of 1-phenyl-3-thiourazole have never been synthesized and we have not, therefore, obtained the direct evidence excluding the possibility that the esters obtained by alkylation are 2-N-esters (X) instead of 3-S-esters (II). Likewise we have not yet synthesized the dialkyl esters (XIII) and shown them to be different from the dialkyl esters (XVII) obtained by the direct alkylation of 1-phenyl-3-thiourazole.





It has seemed to us wise, therefore, to submit the esters assumed to have the constitutions (II) and (XVII) to a number of reactions in order to secure more light on this important question. The first transformation carried out is the oxidation of 1-phenyl-3-thiourazole (VII), 1-phenyl-3-thiomethylurazole (XV), and 1-phenyl-3-thiomethyl-4-methylurazole (XVII). If 1-phenyl-3-thiourazole behaves normally on oxidation with potassium permanganate or hydrogen peroxide we should expect the formation first of a sulfinic acid (VIII) and then of a sulfonic derivative (IX), or even a derivative of sulfuric acid as described by Dr. H. A. Lubs in an article which will appear later. This particular reaction seems to be rather complicated, but Esslinger has isolated a very soluble substance which seems to be a sulfinic acid, and to which we have tentatively assigned the structure (VIII). A silver salt was made which seemed to possess the corresponding formula. Furthermore, Lubs has oxidized (VII) still further and also oxidized the 1-phenyl-3-thio-4-methylurazole corresponding to (VII) and shown definitely that, *when the sulfur at -3- has no alkyl on it, the urazole can be readily oxidized to a corresponding very soluble acid*. This evidence, though preliminary, is of great importance in the following reactions:

The oxidation of (XV) and (XVII), however, is very simple, as they seem to behave like thioethers and yield sulfones. If the methyl derivative, m. p. 175-6°, obtained by the alkylation of 1-phenyl-3-thiourazole or its monobasic salt, had the sulfur free from a methyl group, as in (X), we should expect to get by the final oxidation, just as with (VII), an acid having an oxidized sulfur grouping like (VIII) or (XI). Such an acid should be *very soluble*, at least dibasic and should have at least four oxygen atoms. As a matter of fact the substance obtained is *very insoluble*, behaves like a sulfone, has only three oxygens, is a monobasic acid, forms a mono-silver salt, and behaves in every respect as if it has the structure (XVI). We must conclude, therefore, that the methyl derivative obtained by alkylating 1-phenyl-3-thiourazole, and melting at 175-6°, has the

structure (XV) and is a derivative of (I) or (VII). When the sodium salt of (XVI) is alkylated with methyl iodide a neutral substance is obtained which corresponds in all respects to (XVIII). This same substance is formed by oxidizing the dimethyl derivative (XVII) obtained by methylating 1-phenyl-3-thiourazole (VII) and having the m. p. $95-6^{\circ}$. That this dimethylurazole has the structure (XVII) and not (XIII) is shown by the above reasoning and the fact that one methyl is surely¹ already known to be at -4-. If the other methyl were at -2-, as in (XIII), and the sulfur were free from alkyls, oxidation should give us a *very soluble acid* like (XIV) instead of the *insoluble neutral substance* obtained (XVIII).

It must be decided at present, therefore, that 1-phenyl-3-thiourazole reacts in the enol form (VII) and yields on alkylation the mono- and dialkyl derivatives, (XV) and (XVII), having one methyl on the sulfur at (III) instead of on the nitrogen at -2-. We are planning further experiments to remove the $-SCH_3$ and $-SO_2CH_3$ groups from these urazoles, in order to obtain the corresponding oxyurazoles which have been synthesized by other methods, leaving no doubt as to their constitution.

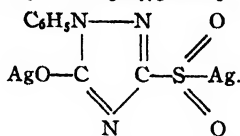
Experimental.

1-Phenyl-5-oxy-4,5-dihydro-3-triazolylsulfonic Acid (VIII).—This compound was made by oxidizing the sodium salt of 1-phenyl-3-thiourazole, either by means of an alkaline solution of potassium permanganate or with a 30% solution of hydrogen peroxide. Both methods gave the same substance which melted at $174-178^{\circ}$.

I. The sodium salt of 1-phenyl-3-thiourazole in a slightly alkaline solution was treated with sufficient potassium permanganate to furnish two oxygen atoms. After all the potassium permanganate had been added, the solution was boiled, then filtered to remove the manganese hydroxide, after which it was evaporated to a small volume and acidified. On cooling 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfonic acid crystallized out.

II. A slightly alkaline solution of the sodium salt of 1-phenyl-3-thiourazole was placed with a smaller sealed tube of 30% hydrogen peroxide in a thick walled glass tube, which was then sealed. By violent shaking the thin walled tube containing the hydrogen peroxide was broken and the two solutions were thoroughly mixed. Hydrogen peroxide in an alkaline solution decomposes rapidly, liberating a large quantity of oxygen which in this case is the active agent. After standing two days the tube was opened and no unchanged 1-phenyl-3-thiourazole was found on the addition of a slight excess of sulfuric acid. The solution was evaporated to a small volume and the same 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfonic acid was obtained as above.

¹ Ber., 36, 3154 (1903).

Di-silver Salt of 1-Phenyl-5-oxy-4,5-dihydro-3-triazolylsulfonic Acid,

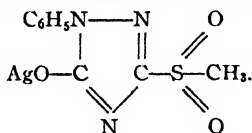
This compound was made by adding silver nitrate to an aqueous solution of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfonic acid. The silver salt precipitated out as a white powder that soon turned gray and when dry was dark brown.

0.3221 g. substance lost 0.0120 g. H_2O at 110° ; 0.5159 g. substance gave 0.2419 g. Ag. Calc. for $\text{C}_8\text{H}_5\text{N}_3\text{O}_3\text{S}_2\text{Ag}_2 \cdot \text{H}_2\text{O}$ (1 mol), 3.94; Ag_2 , 47.17; found: 3.72 and 46.88.

It is not intended by the use of the above formulas to indicate whether the water lost on heating the substance is water of crystallization or of constitution.

1-Phenyl-5-oxy-4,5-dihydro-3-triazolylmethylsulfone (XVI). — This compound was made by oxidizing 1-phenyl-3-thiomethylurazole by means of potassium permanganate as described under the preparation of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfonic acid. This substance differs from 1-phenyl-5-oxy-4,5-dihydro-3-triazolylsulfonic acid in that it separates from the oxidizing mixture on the addition of sulfuric acid. It was easily purified by dissolving it in dilute alkali and precipitating it with sulfuric acid. When pure it melts at $206\text{--}207^\circ$.

1.100 g. substance required 23.1 cc. $N/5$ NaOH; calc., 22.9 cc.

Silver Salt of 1-Phenyl-5-oxy-4,5-dihydro-3-triazolylmethylsulfone,

This silver salt was made by adding silver nitrate to the neutral sodium salt of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylmethylsulfone. The silver salt precipitated out as a white powder, which remained unchanged when dry.

0.2317 and 0.2351 g. substance gave 0.0732 and 0.0732 g. Ag; calc. for $\text{C}_9\text{H}_5\text{N}_3\text{O}_3\text{S}_2\text{Ag}$: Ag = 31.18; found: 31.16 and 31.13.

1-Phenyl-5-oxy-4-methyl-4,5-dihydro-3-triazolylmethylsulfone (XVIII). — This compound was made by treating the neutral sodium salt of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylmethylsulfone with methyl iodide (CH_3I) in boiling alcoholic solution. After heating it for 2 hrs. the reaction mixture was evaporated to a small volume, made alkaline with sodium hydroxide and extracted with chloroform. The chloroform was carefully evaporated, the residue hydrolyzed with hydrochloric acid,

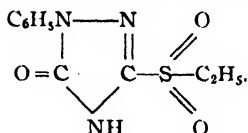
to remove any 1-phenyl-4,5-dihydro-5-methoxy-3-triazolylmethylsulfone that was formed, then made alkaline and extracted with chloroform. The residue obtained after the evaporation of the chloroform was dissolved in a small amount of alcohol, filtered, and slowly poured into water, when the 1-phenyl-5-oxy-4-methyl-4,5-dihydro-3-triazolylmethylsulfone precipitated as a white powder. When pure, this compound melted at $94-95^{\circ}$.

An experiment to determine the ratio of the enol to the keto dimethyl esters gave the following results:¹

Enol (about) 60%

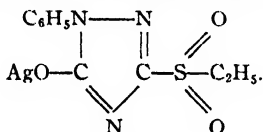
Keto (about) 40%

1-Phenyl-5-oxy-4,5-dihydro-3-triazolylethylsulfone,



This compound was made by the same method used in the preparation of 1-phenyl-4-oxy-4,5-dihydro-3-triazolylmethylsulfone. When pure, this compound is white and melts at $199.5-200^{\circ}$.

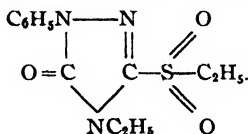
Silver Salt of 1-Phenyl-5-oxy-4,5-dihydro-3-triazolylethylsulfone,



This salt was made by treating a neutral sodium salt of 1-phenyl-5-oxy-4,5-dihydro-3-triazolylethylsulfone with silver nitrate. This salt, when dry, was stable.

0.2526 and 0.4292 g. substance gave 0.0758 and 0.1289 g. Ag; Calc. for $\text{C}_{10}\text{H}_{10}\text{N}_3\text{SO}_3\text{Ag}$: Ag, 29.96; found: 30.00 and 30.03.

1-Phenyl-5-oxy-4-ethyl-4,5-dihydro-3-triazolylethylsulfone,



This compound was made in the same manner as was used in making 1-phenyl-5-oxy-4-methyl-4,5-dihydro-3-triazolylmethylsulfone. The compound was white and melted at 74 to 75° .

The experiment made to determine the ratio of the keto to the enol di-ethyl esters gave the following results:

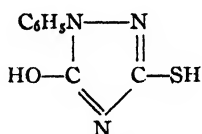
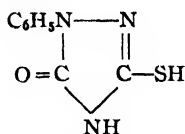
Enol ester (about) 60%

Keto ester (about) 40%

¹ Method described in Marshall's Dissertation J. H. U., 1911.

Conclusions.

From the chemical and conductivity data we can conclude that 1-phenyl-3-thiourazole exists in solution chiefly as an equilibrium mixture represented below:



By means of acids at 125°, under pressure, an alkyl mercaptan can be split off from the products obtained by methylating or ethylating 1-phenyl-3-thiourazole. Hence the assumption that the alkyl group is attached to the sulfur at position 3 seems substantiated further.

Since we obtain *very soluble* acids, apparently sulfinic and sulfonic acids on oxidizing 1-phenyl-3-thiourazole, but obtain *insoluble* sulfone-like substances having two additional oxygen atoms on the oxidation of the alkylation products assumed to be 1-phenyl-3-thioalkylurazoles and 1-phenyl-3-thioalkyl-4-alkylurazoles, we may conclude that these alkyl derivatives have an alkyl on the sulfur at 3, and not on the nitrogen at 2, and that 1-phenyl-3-thiourazole is alkylated in the tautomeric thioenol forms given above.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE, MD.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE VALENCE OF NITROGEN IN AMMONIUM SALTS.

BY WILLIAM A. NOYES AND RALPH S. POTTER.¹

Received November 18, 1914.

During the early years of the development of the theory of valence, many chemists held the view that each element has an unvarying valence. The apparent change of valence in nitrogen from ammonia to ammonium salts, and in phosphorus from phosphorus trichloride to phosphorus pentachloride was explained by calling the ammonium salts and the pentachloride molecular compounds, as distinguished from ammonia and the trichloride, in which the true valence of the elements was supposed to be shown. This view received support from the dissociation of ammonium salts and of phosphorus pentachloride in the gaseous state. Gradually, with the demonstration that phosphorus pentachloride volatilizes in part unchanged, that phosphorus pentafluoride, PF_5 , has a vapor density corresponding to its formula and, in general, that dissociation in the gaseous

¹ Presented in abstract before the American Philosophical Society, April 24, 1914. This paper is also an abstract of a thesis presented to the Graduate Faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

state does not correspond to any rational distinction between unitary and molecular compounds, the view that elements may show a varying valence in their compounds and that nitrogen and phosphorus are sometimes trivalent and sometimes quinquivalent, come to be generally accepted.

More recently, Werner¹ has proposed a modified molecular formula for ammonium chloride, $H_3N \cdots HCl$. By this formula he intends to indicate that in the ammonium salts the nitrogen atom retains a normal valence of three, but that the nitrogen atom of the ammonia and the hydrogen atom of the hydrochloric acid are held together by secondary ("Neben") valences, the hydrogen and chlorine of the acid retaining essentially the same relation to each other as in the free acid.

An amino acid may, theoretically, assume in the aqueous solution the following forms: *a*, the free acid, $R \begin{matrix} \diagup CO_2H \\ \diagdown NH_2 \end{matrix}$; *b*, a cyclic salt, $R \begin{matrix} \diagup CO \\ \diagdown NH_3 \end{matrix} O$,

or according to Werner, $R \begin{matrix} \diagup CO - O \\ \diagdown NH_2 - H \end{matrix} \vdots$; *c*, a bimolecular or polymolecular

salt formed by the union of two or more molecules, $R \begin{matrix} \diagup CO_2 - H_3N \\ \diagdown NH_3 - O_2C \end{matrix} R$;

d, the ions of the acid group $R \begin{matrix} \diagup CO_2^- \\ \diagdown NH_2 \end{matrix}$ and H^+ ; *e*, the ions of the base,

$R \begin{matrix} \diagup CO_2H \\ \diagdown NH_3^+ \end{matrix}$ and OH^- ; *f*, the double, amphoteric ion, $R \begin{matrix} \diagup CO_2^- \\ \diagdown NH_3^+ \end{matrix}$.

The "inner salt" structure was first proposed by Erlenmeyer and Siegel² in 1875. Ten years later Ostwald³ noticed that solutions of glycoll, $CH_2NH_2CO_2H$, have a very low molecular conductivity and that this is only slightly increased by dilution. He states that in its behavior it is more like a neutral salt than an acid. In 1891 Marckwald⁴ called attention to the fact that amino acids of the aliphatic series react only slowly with the mustard oils, while other primary amines react quite readily. Since the amino acids react easily in alkaline solutions, he held that the acids are, in reality, inner salts. Sakurai⁵ attempted to substantiate the "inner salt" structure on their preparation from halogen derivatives of the acids and on the resistance which amino acids offer to the formation of acid chlorides. Walker⁷ points out that conductivity determinations

¹ See *Neuere Anschauungen auf dem Gebiet der anorganischen Chemie*, 1905, p. 96.

² "Zwitterion."

³ *Ann.*, 176, 349 (1875).

⁴ *J. prakt. Chem.*, 32, 369 (1885).

⁵ *Ber.*, 24, 3278 (1891).

⁶ *Proc. Chem. Soc.*, 10, 90 (1894).

⁷ *Ibid.*, 10, No. 139 (1895).

tell us very little about the structure of glycocoll, but that, since the conductivity of phenylglycocoll, $C_6H_5NHCH_2CO_2H$, is greater than that of acetic acid, it must contain a carboxyl group which ionizes. Tilden and Forster¹ showed that the amino group of amino acids may be replaced by chlorine by the action of nitrosyl chloride, and considered this an argument against the inner salt formation. Somewhat later Carrara and Rossi² based an argument for the inner salt structure on the conductivity of betaine hydrochloride, $(CH_3)_3NCICH_2CO_2H$. From the values found they considered that the salt was almost completely hydrolyzed to hydrochloric acid and betaine, $(CH_3)_3NCH_2CO$. Winkelblech³ points out,



however, that if betaine hydrochloride is in reality hydrolyzed the conductivity of the solution should be the same as that of the equivalent amount of hydrochloric acid, while both Bredt's measurements and those of Carrara and Rossi gave a conductivity scarcely more than one-half as great. There can be no doubt, of course, that the anhydride of betaine, $(CH_3)_3NCH_2CO_2$, has the structure of a salt, but no one seems to have determined whether this is monomolecular or dimolecular. Walker⁴

has shown, however, that aminoacetic acid, $CH_2 \begin{array}{l} \diagup CO_2H \\ \diagdown NH_2 \end{array}$, is monomolecular

in aqueous solutions. Our results, given below, indicate that a solution of an amino acid which gives no inner salt may still contain the acid mostly in the monomolecular form.

Winkelblech⁵ discusses the hydrolysis of an amino acid on the basis of conductivity data for weak acids, weak bases and water. It does not seem possible from conductivity data, however, to determine whether the

acid is in the form of an inner salt, $R \begin{array}{l} \diagup CO_2 \\ \diagdown NH_2 \end{array}$, in the unionized state,

$R \begin{array}{l} \diagup CO_2H \\ \diagdown NH_2 \end{array}$ or $R \begin{array}{l} \diagup CO_2H \\ \diagdown NH_3OH \end{array}$, in the form of the double, amphoteric ion

$R \begin{array}{l} \diagup CO_2^- \\ \diagdown NH_3^+ \end{array}$, or in the form of a bimolecular salt, $R \begin{array}{l} \diagup CO_2-NH_3 \\ \diagdown NH_3-CO_2 \end{array} R$. The

hydrogen and hydroxyl ions of the amphoteric form would, of course, combine to form water and if the acid and basic functions were of equal "strength" the solution would react neutral. None of these forms would show any conductivity and, while the bimolecular form could be disting-

¹ *Chem. News*, 71, 239 (1895).

² *Atti R. Accad. Lincei*, [5] 6, 208 (1897).

³ *Z. physik. Chem.*, 36, 590 (1901).

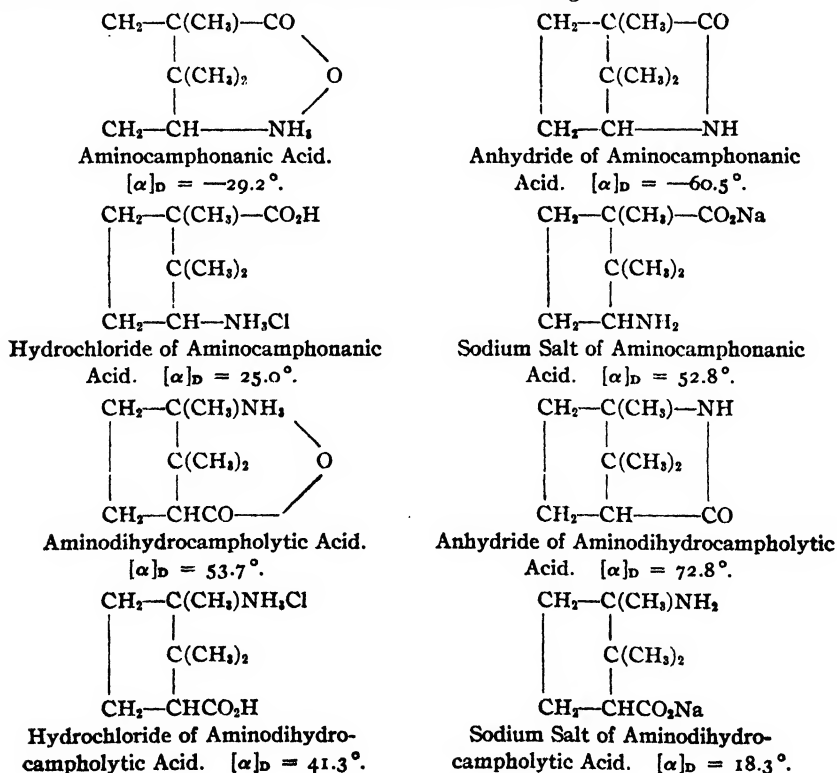
⁴ *Proc. Chem. Soc.*, 10, 94 (1894).

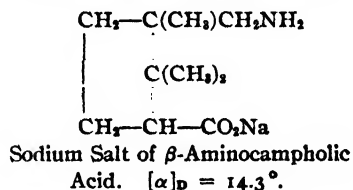
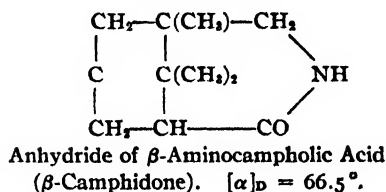
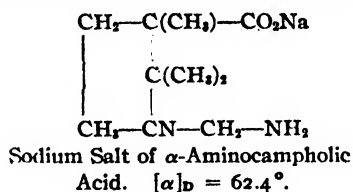
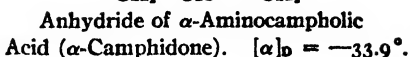
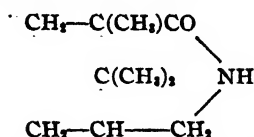
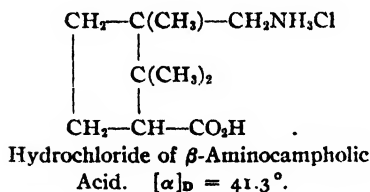
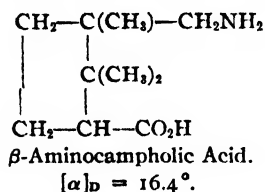
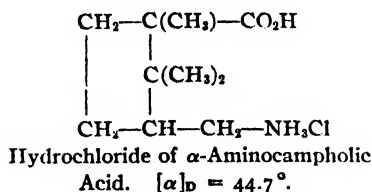
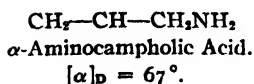
⁵ *Loc. cit.*

uished from the others by a determination of the molecular weight, it is not clear how any of the ordinary physical methods could be used to distinguish between the three forms, $R \begin{matrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{NH}_2 \end{matrix}$, $R \begin{matrix} \diagup \text{CO}_2 \\ \diagdown \text{NH}_3 \end{matrix}$, and $R \begin{matrix} \diagup \text{CO}_2^- \\ \diagdown \text{NH}_3^+ \end{matrix}$.

The form $R \begin{matrix} \diagup \text{CO}_2\text{H} \\ \diagdown \text{NH}_3\text{OH} \end{matrix}$ would have a higher molecular weight and might, possibly, be distinguished from the other three by that means, but it could not be distinguished by conductivity measurements. It does not seem to us that the ordinary equations for hydrolysis, which Winkelblech attempts to apply, could be used in a complex case of this sort.

From the above summary it would seem that the evidence with regard to inner salt formation is not altogether satisfactory and light upon the question from an entirely different point of view is welcome. We think that we have secured this from a study of the specific rotations of a series of amino acids from camphor. The formulas and names of the compounds are given below. To bring out the relationships more clearly the specific rotations given for the salt are calculated to the basis of one gram of the free acid in 1 cc. of the solution instead of for one gram of the salt.



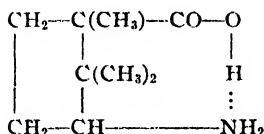


It will be noticed that the aminocamphonic acid and aminodihydrocampholytic acid are represented as having a cyclic or inner salt structure, while the aminocampholic acids are both represented as having an open structure. The evidence for these structures is based on the specific rotation of the compounds. The rotation of the sodium salt and hydrochloride of aminocamphonic acid are to the right while that of the anhydride, which is undoubtedly cyclic in structure, is to the left. The ammonium salt is also left handed, indicating a cyclic structure similar to that of the anhydride. The sodium salt and hydrochloride of aminodihydrocampholytic acid are right handed. The free acid and anhydride are also right handed, but with a considerably increased rotation. The sodium salt and free α -aminocampholic acid are both right handed with rotations closely alike, indicating that each has an open structure, but the anhydride, which certainly has a cyclic structure, is left handed and has a rotation very closely like that of the aminocamphonic acid, indicating again very clearly that the latter has a cyclic structure and that each compound contains a cycle of six atoms. The sodium salt of β -aminocampholic acid and the free acid also correspond closely in rotation, indicating

an open structure for both, while the hydrochloride and anhydride have a considerably greater rotation, as is the case with both the free aminodihydrocampholytic acid and its anhydride.

All of these observations are consistent with the hypothesis that aminodihydrocampholytic and aminocamphonan acid form cyclic salts containing cycles of six atoms, while the aminocampholic acids do not form such salts, because, if formed, they would contain cycles of seven atoms. It seems difficult to find any other simple explanation for the observations.

The results also point very strongly to the formula for ammonium salts which represents them as containing quinquivalent nitrogen and against Werner's formula. According to Werner's formula the free aminocamphonan and aminodihydrocampholytic acids would contain cycles of seven atoms,



Such a formula is quite inconsistent with all that we know about the ease with which rings of five and six atoms are formed and the comparative rarity of seven-atom rings. It is also inconsistent with the close agreement between the rotation of the aminocamphonan acid and that of the anhydride of α -aminocampholic acid. We know that the latter compound contains a six-atom ring.

Determinations of the molecular weights in aqueous solutions by the freezing point method have shown that all four of the amino acids are monomolecular in such solutions.

The following table brings out in a striking way the relations which have been found. The rotations are calculated from results obtained with solutions containing from 2.5 to 10% of the substances examined and are given on the basis of the amount of free amino acid corresponding to the compound which was present. Thus $[\alpha]_D$ for the hydrochloride of aminocamphonan acid (*i. e.*, the rotation in a 10 cm. tube of 1 g. in 1 cc.) is 25.0° but the rotation in the table is given as 30.3°, which is the calculated rotation for 1 g. of the free acid in 1 cc., after conversion into the hydrochloride.

| | HCl salt. | Free acid. | HCl salt + 1 mol NaOH. | HCl salt + 2 mols NaOH. | Anhy- dride. |
|------------------------------------|--------------|---------------|---------------------------------|----------------------------------|-----------------|
| Aminocamphonan acid..... | 30.3° | -29.2° | -28.8° | 55.4° | -60.5° |
| Aminodihydrocampholytic acid..... | 50.1° | 54.7° | 54.0° | 20.5° | 72.8° |
| α -Aminocampholic acid..... | 53.3° | 67.0° | 62.4° | 65.6° | -33.9° |
| β -Aminocampholic acid..... | 49.5° | 16.4° | 16.7° | 15.2° | 66.5° |

The free acids have, in each case, nearly the same rotation when prepared by the addition of one mol of sodium hydroxide to one mol of the hydro-

chloride, as when the pure acid is dissolved directly in water. The addition of a second mol of sodium hydroxide causes a large change in the rotations of aminocamphonanic and aminodihydrocampholytic acids, evidently because the cyclic structure of the inner salt is broken down by the formation of the sodium salt, but no such change is observed with the campholic acids.

Experimental.

Aminocamphonanic Acid, C_8H_{14} $\begin{cases} CO_2H \\ NH_2 \end{cases}$.—The hydrochloride of amino-

camphonanic acid was prepared as previously described.¹ One hundred grams of the hydrochloride were dissolved in water and a solution of sodium hydroxide added till the reaction was faintly alkaline to phenolphthalein after boiling a small portion in a test tube. The solution was then evaporated to about 100 cc. and the free amino acid obtained was filtered off and was recrystallized by dissolving in water and evaporating the solution. The yield of the crude acid was 72 g., about 82% of the theory. It is possible to recover the remainder of the acid as hydrochloride from the mother liquors. The free acid is about equally soluble in hot and cold water. Hoogewerf and Van Dorp² report a melting point of 260°. If heated rather rapidly we find that it sublimes without melting at a temperature above 300°. It is probable that the melting point reported by Hoogewerf and Van Dorp was found by heating slowly, which causes a partial conversion into the anhydride. The latter melts at 203°. Because of the melting point reported by the authors mentioned, and because of the left-handed rotation, which seemed to us, at first, anomalous for a derivative of dextrocamphoric acid, the mother liquors from the preparation of the aminocamphonanic acid were very carefully examined for a possible isomer, but none was found.

The aqueous solution of aminocamphonanic acid, 10 g. in 100 cc. of the solution, gave a specific rotation $[\alpha]_D^{25} = -29.2^\circ$.

The molecular weight was determined with a sample which had been recrystallized six times from water, twice more than was necessary to remove all of the chlorine. A solution of the acid was mixed with ice, from distilled water, which had been broken to pieces the size of a pea and the mixture was placed in a Dewar bulb. After equilibrium was reached and the temperature had been taken, 20 cc. of the clear solution were drawn off and evaporated and the residue dried to constant weight on the water bath. The results were:

Subst., 0.304; H_2O , 16.6; depression, 0.194; mol. wt. found, 173. Calc. for $C_8H_{14}CO_2NH_2$, 171.

¹ *Am. Chem. J.*, **16**, 507 (1894). Formerly called aminolauronic acid. See *THIS JOURNAL*, **34**, 1067 (1912).

² *Ibid.*, **16**, 506 (1874), footnote.

The Anhydride of Aminocamphonic Acid, C_8H_{14} $\begin{array}{c} \diagup CO \\ | \\ \diagdown NH \end{array}$, has been

prepared¹ by distilling a mixture of the hydrochloride and lime. The following method gives a nearly quantitative yield and avoids the use of a high temperature: Ten grams of the hydrochloride, 6 g. (1.5 mol) of fused sodium acetate, and 20 cc. of acetic anhydride were boiled gently in a long necked flask for about 10 min. After cooling, 10% excess of a strong solution of sodium hydroxide was added and the mixture heated on the water-bath till the liquid layer which formed at first on top was changed to a solid. The liquid layer probably consisted in part of the acetyl derivative of the anhydride, but this was not examined further. After cooling, the anhydride was separated by two extractions with ether. After two crystallizations from petroleum ether it melted quite sharply at 203° .²

$[\alpha]_D^{29} = -60.5$, 1 g. in 10 cc. of absolute alcohol and $[\alpha]_D^{28} = -60.6^\circ$, 0.05 g. in 10 cc. of water. Noyes and Taveau³ found $[\alpha]_D^{26} = -60.1^\circ$ for a 10% alcohol solution.

Subst., 0.373, 0.750; H_2O , 20.9, 20.1; depression, 0.208°, 0.432°; mol. wt. found, 157, 159. Calc. for C_8H_{14} $\begin{array}{c} \diagup NH \\ | \\ \diagdown CO \end{array}$: 153.

Hydrolysis of Aminocamphonic Acid Anhydride.—The anhydride was not hydrolyzed by heating with water for three days in a water-bath. Heating for three days in the water-bath with an excess of sodium hydroxide was also without effect, but when 3 g. of the anhydride were heated for 10 hrs. with 20% hydrochloric acid the solution deposited crystals of

the hydrochloride of aminocamphonic acid, C_8H_{14} $\begin{array}{c} \diagup CO_2H \\ | \\ \diagdown NH_3Cl \end{array}$, on cooling.

This gave $[\alpha]_D^{24} = 24.9^\circ$, proving that there is no inversion of the acid either in the formation of the anhydride or in its hydrolysis.

Acetyl Derivative of Aminocamphonic Acid Anhydride, C_8H_{14} $\begin{array}{c} \diagup CO \\ | \\ \diagdown NC_2H_5O \end{array}$.

—This was prepared by boiling a mixture of 6 g. of aminocamphonic acid hydrochloride, 3.5 g. of sodium acetate and 12 cc. of acetic anhydride for 10 min. After cooling and adding enough sodium hydroxide to nearly neutralize the acetic acid and excess of acetic anhydride, the mixture was extracted with petroleum ether and the extract washed with water to remove free acid. After drying with sodium sulfate and distilling away the

¹ THIS JOURNAL, 34, 62 (1912).

² Am. Chem. J., 16, 507 (1894).

³ Ibid., 32, 288 (1904).

petroleum ether, a slightly yellow oil was obtained. This was distilled and the portion boiling at 260–262° was analyzed:

Calc. for $C_8H_{14}CONC_2H_5O$: N = 7.16; found: 7.05; $[\alpha]_D = +72.7^\circ$, 0.544 g. in 5 cc. of alcohol.

The substance gave aminocamphonanic anhydride melting at 201–203° by hydrolysis with sodium hydroxides.

Nitroso Derivative of Aminocamphonanic Anhydride, C_8H_{14}

—This was prepared by Bredt,¹ but he did not determine the specific rotation.

We found $[\alpha]_D^{24^\circ} = 153^\circ$; 0.25 g. in 10 cc. of alcohol.

It is interesting to notice that both the acetyl and the nitroso group change the negative rotation of the anhydride to a positive, the nitroso group producing a much larger effect than the acetyl group.

Cyanocamphonanic Acid, C_8H_{14}

α -camphoramidic acid, C_8H_{14}

to the method of Hoogewerf and Van Dorp.² This gave about the same yield of crude acid which they obtained, namely, about 50%. It was thought, since the hydrochloride of the α -isoimide obtained by treating the α -camphoramidic acid with acetyl chloride is very easily hydrolyzed by water to the α -camphoramidic acid, that perhaps by suspending the isoimide hydrochloride in petroleum ether and passing in dry ammonia gas, the yield could be increased. The following procedure was used: 12.5 g. of α -camphoramidic acid and 50 g. of acetyl chloride were placed in a flask which was attached to a reflux condenser. The flask was heated on the water bath. A solution is first formed and in about two minutes the contents of flask apparently become solid. The flask and material were then cooled, the material filtered and the solid washed with carbon disulfide. Up to this point the method of procedure was just the same as given by the above mentioned investigators. Instead of adding the isoimide hydrochloride to 20% ammonia, as they did, it was shaken with petroleum ether and a slow stream of dry ammonia gas was passed through the mixture until saturation was reached. A dilute solution of ammonia was added to dissolve the ammonium salts, and from the aqueous solution the cyanoacid was precipitated with dilute hydrochloric acid. The hydrochloric acid solution must be added drop by drop or the cyanoacid will be precipitated as a gummy mass. The crystalline acid was filtered

¹ *Ber.*, 35, 1291 (1902).

² *Rec. trav. chim.*, 14, 261 (1895).

and, after drying, was weighed. 10 g., or 84%, of the theory was obtained. For purification two methods were used, one by recrystallization from hot water, which was the method used by Hoogewerf and Van Dorp, the other, by dissolving the acid in dilute ammonium hydroxide and precipitating it with dilute hydrochloric acid. By the first method from 5 g. of the crude acid 2.4 g. of acid, melting sharply at 121° , were obtained. This is the melting point found by the above mentioned investigators. By the second method, 3.1 g. of the pure product were obtained from 5 g. of the crude acid. This method is also to be preferred on account of its greater ease of manipulation.

$[\alpha]_D^{26} = 67.3^{\circ}$, 1 g. in 10 cc. of alcohol. Hoogewerf and Van Dorp¹ found exactly the same for a 6% alcoholic solution.

α -Aminocampholic Acid Hydrochloride, C_8H_{14} $\begin{cases} CO_2H \\ CH_2NH_2Cl \end{cases}$.—The only

variation from the method of preparation of Hoogewerf and Van Dorp² or Rupe and Splittgerber³ was that a somewhat larger portion of sodium was used in the reduction. 5 g. of cyanocamphonan acid were dissolved in 50 cc. of absolute alcohol and 15 g. of sodium were added in small portions, the flask being connected to a reflux condenser. During the addition of the sodium about 20 cc. more of alcohol were added. After all the sodium had dissolved water was added and the solution was evaporated until the odor of alcohol was no longer given. From this point on a method of separation and purification of the hydrochloride entirely different from that of Rupe and Splittgerber³ was used. Hydrochloric acid in slight excess was added to the cold solution and it was then extracted with ether in order to remove any unchanged cyanoacid. Upon evaporation of the ether solution it was found that about 1 g. of cyanoacid was obtained. This was used in subsequent reductions. The hydrochloric acid solution was evaporated to dryness and the residue ground up in a mortar with alcohol. The alcohol was filtered, diluted, with water and the alcohol was evaporated. The brown turbidity of the solution was then removed by filtering twice through powdered animal charcoal. The clear solution was then evaporated on the water bath until crystals started to form, when it was removed and allowed to cool and filtered. The very slightly brown crystals were dissolved in the minimum amount of hot water, filtered again through animal charcoal and after cooling, the pure white, needle-like crystals were filtered off, dried, and a melting point taken. It was found to be $248-250^{\circ}$. A portion was again recrystallized and the same melting point was given.

¹ *Rec. trav. chim.*, **14**, 26 (1895).

² *Ibid.*, **14**, 261 (1895).

³ *Ber.*, **40**, 4313 (1907).

Rupe and Splittgerber¹ give the melting point as 247–248°. The specific rotation, which had never been taken before, was determined.

$[\alpha]_D^{24} = 44.7^\circ$; 0.5 g. in 10 cc. of a solution in water.

Calc. for $C_8H_{14}(CO_2H)CH_2NH_2HCl$: Cl = 16.00; found: Cl, 16.17.

α -Aminocampholic Acid, C_8H_{14} $\begin{matrix} \diagup CO_2H \\ \diagdown CH_2NH_2 \end{matrix}$.—An attempt was made

to prepare the free acid from its hydrochloride in the same manner that aminocamphonan acid is prepared from its hydrochloride, but the free acid was apparently more soluble than sodium chloride and this method was abandoned. Instead, the hydrochloride was dissolved in water and sodium hydroxide added until an outside test with phenolphthalein showed a very faint alkaline reaction. The solution, after filtering, was evaporated to dryness and the residue was ground up in a mortar with alcohol, the alcohol filtered, diluted and partially evaporated. The slightly turbid solution was filtered through charcoal and then the solution was evaporated until only a few cubic centimeters of liquid were left, a large mass of crystals having separated during the evaporation. The crystals were filtered off and recrystallized by evaporation of the water solution, the acid being practically as soluble in cold as in hot water. This was repeated three times more and the acid then showed no trace of chlorine. The molecular weight was determined with this sample. Heated in a capillary tube no melting point was obtained but considerable decomposition took place between 300° and 320°, depending upon the rate of heating.

$[\alpha]_D^{26} = 67.0^\circ$; 0.207 g. in 10 cc. of solution.

Subst., 0.418, 0.585; H_2O , 15.6, 18.4; depression, 0.251°, 0.297°; mol. wt. found,

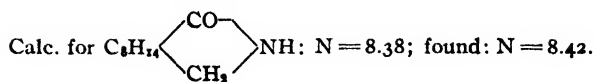
196, 197. Calc. for C_8H_{14} $\begin{matrix} \diagup CH_2-NH_2 \\ \diagdown (CO_2H) \end{matrix}$: 185.

α -Camphidone, C_8H_{14} $\begin{matrix} \diagup CO \\ \diagdown CH_2 \end{matrix} > NH$.—This was prepared from the

hydrochloride of α -aminocampholic acid in precisely the same manner as the anhydride of aminocamphonan acid was prepared from the hydrochloride of aminocamphonan acid. After making the acetic anhydride solution alkaline with sodium hydroxide the same liquid layer was observed on the surface that was observed in the preparation of the above mentioned anhydride. This was very likely the acetyl derivative, but no attempt was made to isolate it. Practically a theoretical yield of the anhydride was given. It melts at 229–231°. Recrystallizing once from petroleum ether gave a pure product melting at 230–231°.

$[\alpha]_D^{26} = -33.9^\circ$; 0.5 g. in 10 cc. alcohol solution. Rupe and Splittgerber¹ give $[\alpha]_D = -37.2^\circ$ in a 10% solution in benzene.

¹ *Ber.*, 40, 4313 (1907).



Nitroso Derivative of α -Camphidone, C_8H_{14} $\begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CH}_2 \diagup \end{array}$ NNO.—The

α -camphidone was dissolved in hydrochloric acid (1 : 4) and a sodium nitrite solution slowly added. The yellow crystals formed were filtered, dried and recrystallized from hot alcohol. The lemon yellow, needle-like crystals gave a melting point of 125–126°. The product given by a second recrystallization showed the same melting point.

$$[\alpha]_D^{23} = -59.0^\circ; 0.25 \text{ g. in 10 cc. of alcohol.}$$

From analogy to the well-known nitroso derivatives of aminocamphonanic and dihydroaminocampholytic acid anhydrides, it was not thought necessary to analyze the compound for identification.

Aminodihydrocampholytic Acid, C_8H_{14} $\begin{array}{c} \diagup \text{NH}_2 \\ \diagdown \text{CO}_2\text{H} \end{array}$.—This acid was pre-

pared in the same manner as described by Noyes¹ except that a more elaborate method was followed in recovering the last traces of the acid. The procedure followed was identical with that for the preparation of aminocamphonanic acid from α -camphoramidic acid, except that β -camphoramidic acid was used and, instead of adding sufficient hydrochloric acid to give the acid hydrochloride, only enough was added to give a solution exactly neutral to phenolphthalein. After this point the solution was evaporated until the sodium chloride was starting to come down. The crystals of the amino acid were then filtered off and to the filtrate an excess of hydrochloric acid was added and the whole evaporated to dryness, and the residue extracted with alcohol. Since the dihydroaminocampholytic acid is quite easily esterified, the alcoholic solution was diluted with considerable water and just enough sodium hydroxide solution added to give a solution neutral to phenolphthalein. It was then partially evaporated and the amino acid filtered off. An excess of hydrochloric acid was added to this filtrate and the same procedure followed as above. Since the acid is no more soluble in hot than in cold water and is not soluble in any other solvent it must be purified by dissolving in water and partial evaporation. For ordinary purposes one recrystallization is sufficient. For taking the molecular weight and rotations an acid was used which had been recrystallized six times, two more times than was necessary to free it from traces of chlorine.

$$[\alpha]_D^{25} = 54.7^\circ; 0.5 \text{ g. in 10 cc. of water solution. Noyes and Phillips}^2 \text{ give } [\alpha]_D =$$

¹ *Am. Chem. J.*, 16, 503 (1894).

² *Ibid.*, 24, 290 (1900).

53.7° for the saturated solution (about 7.5%). Subst., 0.415, 0.613; H₂O, 20.5, 21.2; depression, 0.199, 0.278; mol. wt. found, 187, 191; Calc. for C₈H₁₄ $\begin{matrix} \text{NH}_2 \\ \diagup \\ \text{CO}_2\text{H} \end{matrix}$: 171.

Aminodihydrocampholytic Acid Hydrochloride, C₈H₁₄ $\begin{matrix} \text{NH}_3\text{Cl} \\ \diagup \\ \text{CO}_2\text{H} \end{matrix}$.—A

few grams of the free acid were shaken with a few cc. of water and sufficient hydrochloric acid was added to give a green color to methyl violet paper. The solution was then partially evaporated and upon allowing to cool the hydrochloride separated. It was filtered and recrystallized from hot water. A melting point of 262–263° was found. Recrystallizing again gave a product melting at 261–262°, which is the same as that reported by Noyes.¹

$[\alpha]_D^{26} = 41.3^\circ$; 1 g. in 10 cc. of water solution.

Aminodihydrocampholytic Acid Anhydride, C₈H₁₄ $\begin{matrix} \text{NH} \\ \diagup \\ \text{CO} \end{matrix}$.—This sub-

stance was prepared either by treating the free acid with acetic anhydride or by treating the hydrochloride of the acid with sodium acetate and acetic anhydride and subsequently heating the mixture with an excess of sodium hydroxide. In the latter method it is probable that the acetyl derivative is formed, as the similar liquid layer was always formed on addition of the excess of sodium hydroxide to the acetic anhydride solution. The latter method of preparation has the advantage of allowing quite impure hydrochloride to be used. The melting point, 188–189°, and the specific rotation, $[\alpha]_D^{30} = 72.8^\circ$, have already been published.²

Nitroso Derivative of Aminodihydrocampholic Acid Anhydride,

C₈H₁₄ $\begin{matrix} \text{N NO} \\ \diagup \\ \text{CO} \end{matrix}$.—Since the rotation of this substance had never been

reported it was thought desirable to obtain it. It was prepared according to a method previously reported.²

$[\alpha]_D^{26} = -83.3^\circ$; 0.25 g. in 10 cc. of absolute alcohol solution.

Cyanodihydrocampholytic Acid.—Hoogewerf and Van Dorp³ prepared this acid in just the same manner that they prepared the cyanocamphonanamic acid. Rupe and Splittgerber⁴ proceeded in essentially the same manner. Starting with 12.5 g. of β-camphoramidic acid and proceeding in precisely the same manner as in the preparation of the cyanocamphonanamic acid, 9.5 g. of crude acid were obtained, which is an 80% yield. There was not nearly as much tendency to form a gummy pre-

¹ *Am. Chem. J.*, **16**, 504 (1894).

² Noyes and Potter, *THIS JOURNAL*, **34**, 1072 (1912).

³ *Rec. trav. chim.*, **14**, 267 (1895).

⁴ *Ber.*, **40**, 4313 (1900).

cipitate as was noted in the case of the cyanocamphonic acid. The crude acid was purified by dissolving in 8% ammonia and precipitating with hydrochloric acid. One such procedure sufficed to bring the melting point up to 109–110°. A portion was recrystallized again in the same manner but no change in the melting point was observed. The above is the melting point observed by Hoogewerf and Van Dorp.¹

$[\alpha]_D^{22} = 25.3^\circ$; 0.6 g. in 10 cc. of alcohol solution. Hoogewerf and Van Dorp give the specific rotation $[\alpha]_D = 18.12^\circ$ for a 6% alcohol solution.

Since they purified their acid by recrystallization from hot water, in order to clear up the remote possibility of this causing the difference in the rotation, some of the crude acid was purified by their method, but a rotation taken after the fourth recrystallization, gave a value $[\alpha]_D = 25.2^\circ$ and after the fifth recrystallization $[\alpha]_D = 25.3^\circ$, so there is little doubt but that this is the correct value.

β -Aminocampholic Acid Hydrochloride, C_8H_{14} $\begin{matrix} \nearrow NH_3Cl \\ \searrow CH_2CO_2H \end{matrix}$.—Starting

with cyanodihydrocampholytic acid the procedure for the preparation, separation, and purification of this substance was the same as the preparation of the α -aminocampholic acid hydrochloride. It was found, however, that the reduction in the case in hand was not as complete as with the cyanocamphonic acid. It was found more advisable to simply separate the unchanged cyanoacid by extraction of the acid solution with ether than to use more sodium and alcohol. The β -aminocampholic acid hydrochloride is somewhat less soluble than its isomer and hence it is more easily purified. After two recrystallizations its melting point was 218–220°.

$[\alpha]_D^{26} = 41.3^\circ$; 0.5 g. in 10 cc. of water solution.

β -Aminocampholic Acid, C_8H_{14} $\begin{matrix} \nearrow NH_2 \\ \searrow CH_2CO_2H \end{matrix}$.—About 5 g. of the pure

hydrochloride were dissolved in the minimum amount of water and sufficient strong sodium hydroxide solution (3 cc. = 1 g.) was added to give a solution neutral to phenolphthalein. The free acid, which was precipitated, was filtered, dissolved in hot water, partially evaporated and filtered. This was repeated until a substance free from chlorine was obtained, three recrystallizations in all being required.

$[\alpha]_D^{26} = 16.4^\circ$; 0.25 g. in 10 cc. of solution.

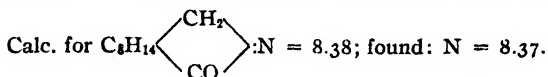
Subst., 0.318, 0.389; H_2O , 22.1, 21.8; depression, mol. wt. found, 199, 197. Calc. for

C_8H_{14} $\begin{matrix} \nearrow CO_2H \\ \searrow CH_2NH_2 \end{matrix}$: 185.

β -Camphidone, C_8H_{14} $\begin{matrix} \nearrow CH_2 \\ \searrow CO \end{matrix}$ $\rangle NH$.—This compound was prepared from

¹ *Rec. trav. chim.*, 14, 267 (1895).

the β -aminocampholic acid hydrochloride in just the same manner as the α -camphidone was prepared from the α -aminocampholic acid. A melting point of $234-235^\circ$ was found and a specific rotation $[\alpha]_D^{24} = 63.2^\circ$; 0.25 g. in 5 cc. of alcohol solution. Rupe and Splittgerber¹ report a melting point of 225° and its specific rotation $[\alpha]_D = 66.5^\circ$ for a 10% solution in benzene. An analysis of the compound was made.



Nitroso Derivative of β -Camphidone, $C_8H_{14} \begin{array}{c} \diagup CH_2 \diagdown \\ \diagdown CO \diagup \end{array} N NO$.—The β -

camphidone was dissolved in dilute hydrochloric acid (1 : 4) and a sodium nitrite solution was added. The yellow precipitate was filtered and recrystallized from alcohol two times, when a melting point of $164-165^\circ$ is given. A portion recrystallized a third time showed the same melting point.

$[\alpha]_D^{23} = 103^\circ$; 0.25 g. in 10 cc. of solution.

Summary.

It is shown in this paper that the specific rotations of some amino derivatives of camphoric acid are consistent with the view that those amino acids which can form cyclic salts containing quinquivalent nitrogen and

a ring of six atoms form salts having the general formula $R \begin{array}{c} \diagup CO \diagdown \\ \diagdown NH_3 \diagup \end{array} O$

in aqueous solutions. Amino acids which would give a ring of seven atoms in forming a cyclic salt appear to exist in solution as compounds of the

form, $R \begin{array}{c} \diagup CO_2H \\ \diagdown NH_2 \end{array}$. These relations furnish strong evidence that nitrogen

is in reality quinquivalent in ammonium salts and that the hydrogen of the acid combines with the nitrogen instead of remaining combined with the acid radical, as Werner has supposed.

Several new compounds have been prepared and the specific rotations of a number of known compounds have been determined.

URBANA, ILLINOIS.

[FROM THE RESEARCH LABORATORY OF PARKE, DAVIS & CO.]

ON THE PRESENCE OF HISTIDINE-LIKE SUBSTANCES IN THE PITUITARY GLAND (POSTERIOR LOBE).

By T. B. ALDRICH.

Received November 5, 1914.

In 1896, A. Kossel discovered among the cleavage products of sturine

¹ Ber., 40, 4313 (1907).

a line. Later this compound was found among the cleavage products of complex proteins when these were subjected to hydrolytic or tryptic digestion.³

According to Pauly,⁴ a solution of histidine made alkaline with sodium carbonate gives a very beautiful diazo reaction with diazobenzene sulfonic acid, which is deep cherry-red in dilutions of 1 : 20,000 and still markedly red in 1 : 100,000. Furthermore it is stated that, with the exception of tyrosine, no other cleavage product from protein, among a large number tested, gives such a color reaction, and that not only can histidine be detected by means of this reaction when mixed with other cleavage products, but also when in the original protein before cleavage, where it is united with other groups, providing the tyrosine is removed or changed so as not to react with this reagent.

As far as investigated by Pauly no other proteid cleavage product outside of histidine and tyrosine gives this reaction. Nearly all give a lemon yellow color in soda solution; such color being given, according to Pauly, by glycocol, alanine, leucine, valine, serine, lysine, ornithine, arginine, asparagine, glutamic acid, cystine, and hippuric acid, while with pyrrolidine carboxylic acid and tryptophane no reaction is given. Glucosamine, phenylalanine and oxyproline carboxylic acid, as well as the cleavage products obtained by Skraup⁵ from caseine were not available to Pauly, but he states that it is not to be supposed that an exception would be found among these products.⁶

In the diazo-reaction we have, therefore, a positive means of determining whether protein or protein cleavage products contain histidine or tyrosine, especially as these bodies give a positive reaction where Millon's test is practically negative. The greatest importance seems, however, to lie in the fact that this reaction shows the presence of histidine and tyrosine in protein-like combination. Whenever a protein substance gives Pauly's reaction, then either tyrosine or histidine has been demonstrated among the hydrolytical cleavage products of this protein; while in other proteins where the diazo-reaction was negative these bodies were absent.

Pauly's method⁷ of preparing diazobenzene sulfonic acid (which should be prepared fresh every time) and his directions for applying the test are as follows:

¹ *Z. physiol. Chem.*, 22, 182 (1896).

² Hedin, *Ibid.*, 22, 191 (1896).

³ Kutscher, *Ibid.*, 25, 195 (1898).

⁴ *Ibid.*, 42, 513 (1904).

⁵ *Ber.*, 37, 3 (1896).

⁶ My experience with Pauly's histidine test has shown me that other bodies besides tyrosine and histidine respond to this test, giving a reddish color that might be confusing. Among the bodies tested may be mentioned *p*-oxyphenylethylamine and β -iminazoyl-ethylamine.

⁷ Pauly, *Loc. cit.*

1. Preparation of Diazobenzenesulfonic Acid.—Two grams of finely powdered sulfanilic acid are mixed with 3 cc. of water and 2 cc. concentrated hydrochloric acid, forming a thick paste. To this is added in small portions, in less than a minute, cooling after each addition, a gram of potassium nitrite dissolved in 1–2 cc. of water. The sulfanilic acid, for the most part, passes rapidly in solution and there is formed a thick, white crystalline precipitate of diazobenzene sulfonic acid which, after a few minutes, is filtered off by suction and washed with a little cold water. Any unchanged sulfanilic acid does not influence the reaction.

2. Reaction with Histidine.—To the solution to be tested, having demonstrated the absence of tyrosine by Millon's reagent, an excess of sodium carbonate (preferred to caustic soda) is added, and then 3–5 cc. of an alkaline carbonate solution of a few centigrams of the diazobenzene sulfonic acid prepared at the time of testing. Within three minutes at the longest, usually immediately, a dark cherry-red color appears, which even by dilution with many times its volume of water, retains its red color and does not shade into yellow. By acidulating, the color passes into a pure orange color.

Quite recently, K. Inouye,¹ working in Kossel's laboratory, published a method for detecting histidine in the presence of tyrosine, employing the above reaction. According to this investigator, the reaction is also given even when histidine is in combination with the protein molecule, and were it not for the fact that tyrosine, free or attached to protein, gives a very similar red color reaction with diazobenzene sulfonic acid, it would be a comparatively simple matter to detect histidine, just as tyrosine and tryptophane are recognized by color tests.

Since tyrosine gives with diazobenzene sulfonic acid, in alkaline solution, a color reaction that can not be distinguished from that of histidine, Inouye modified the test so as to eliminate the tyrosine from the reaction. This modification was brought about by benzoylating in alkaline soda solution.

If one shakes a solution of tyrosine with a few drops of benzoylchloride until the odor of the chloride has disappeared, after making alkaline with soda solution, the addition of diazobenzene sulfonic acid to the filtrate does not produce the characteristic color. If, on the other hand, one benzoylates histidine by the same process, the color reaction persists.

It was expected, according to Inouye, that this reaction for recognizing histidine would be applicable when histidine was united with protein or other complexes; but this expectation was not realized; for, after benzoylating such bodies, the color reaction could not be obtained, and it was found necessary to hydrolyze these substances either with the help of acids or by digestion with trypsin in order to establish the presence of histidine.

¹ *Z. physiol. Chem.*, 83, 79 (1912).

Having observed several years ago that pituitary preparations, obtained from the anterior lobe, gave a marked histidine reaction, I was led to investigate the posterior lobe, but at that time, no method was known for detecting the presence of tyrosine. On the appearance of Inouye's communication referred to above, I concluded to use his method for detecting the presence of histidine in this lobe, the results of which investigations are given below:

Experimental.

The material employed was the desiccated defatted posterior lobe of the pituitary gland (consisting for the greater part of protein) prepared in the usual way, and a purified product soluble in water. (Three tests were made in all.)

Hydrolysis by Acid.—(1) 0.5 g. of the desiccated product was boiled for 5 hrs. (employing a return condenser) with 100 cc. of water, to which was added 2.5 cc. of concentrated hydrochloric acid. It was then evaporated on the steam bath to a syrupy consistency, taken up in water, an excess of lead oxide added, and the mixture warmed on the steam bath. After cooling it was made alkaline with sodium carbonate solution, filtered, and brought up to 80 cc.

(a) 10 cc. of the above were taken (representing 63 mg. of the original powder), 0.5 cc. saturated sodium carbonate solution and then 3 drops of benzoyl chloride were added and the mixture was agitated until the odor of the chloride had disappeared. It was then filtered and Pauly's test applied as follows:

5 cc. (32 mg.) + 4 drops of sodium carbonate saturated solution + 30 mg. of diazobenzene sulfonic acid either in solid form or dissolved in water. *Color reaction very pronounced.*

(b) 10 cc. + $1\frac{1}{2}$ cc. saturated sodium carbonate solution + 15 drops of benzoyl chloride, etc. *Reaction pronounced but not as strong as by (a).*

(2) 0.5 g. of the perfectly soluble product, treated as by (1). Made up to 80 cc.

(a) 10 cc. taken + $1\frac{1}{2}$ cc. of saturated sodium carbonate solution + 15 drops of benzoyl chloride, etc., etc.

Pauly's reaction pronounced, but less so than the original product.

Without Hydrolysis.—(3) 0.5 g. (perfectly soluble product) dissolved in 25 cc. H_2O , 3 cc. of saturated sodium carbonate solution added then 20 drops of benzoyl chloride. The resulting solution worked up in the usual way, gave a strong Pauly's reaction.

(4) Repeated (3) *Pauly's reaction pronounced.*

Hydrolysis by Trypsin.—(1) 0.2 g. pancreatin was agitated with 40 cc. of a 0.5% sodium carbonate solution.

(a) To 20 cc. of the above was added 0.5 g. of desiccated posterior lobe powder, and a few drops of chloroform. Placed in incubator for about 2 days.

(b) The remaining 20 cc. of (5) was also placed in incubator, a little chloroform being added.

Both (a) and (b) were agitated from time to time.

At the end of 2 days both solutions were evaporated (after neutralizing with hydrochloric acid) to a small volume, made alkaline, then benzoylated and eventually filtered. Both gave pauly's reaction, but the color given by (a) was more intense.

It might be stated at this point that both powders gave Millon's test before as well as after hydrolysis; but that after benzoylating, this reaction was always negative.

In the above experiments I have purposely used a large excess of benzoyl chloride and sufficient sodium carbonate solution to maintain an alkaline reaction. Inouye states that he used only a few drops; but in every case after thorough benzoylating I found even with a large excess of benzoyl chloride that the solution gave a positive reaction. In some instances the color was not as pronounced as one would expect, but this might be accounted for by the larger amount of benzoyl chloride used, or the fact that all was not decomposed, or that the presence of benzoic acid or its salts influenced the same.

One would conclude from the above, if Inouye's observations are correct, that histidine is present in the above preparations, prepared from the pituitary gland, were it not for the fact that the solutions before or after hydrolysis or after benzoylating failed to give in my hands Weidel's reaction as modified by Fisher or Knoop's bromine reaction. Whether we are justified, however, in drawing this conclusion is questionable, for it may be assumed that other bodies are present which interfere with the reaction or that histidine is present in too small an amount.

Under hydrolysis by trypsin the presence of a small amount of histidine in the *control* is explained by its presence in the pancreatin employed.

From (3) without hydrolysis, it would seem that at least one of the histidine-like substances in the pituitary gland (posterior) is not united to protein, for after benzoylating, employing an excess of sodium carbonate, the filtrate gave a strong Pauly's reaction. It is quite probable that we have a free and possibly a combined histidine or histidine-like compound. We are also confronted by the possibility of several substance of this nature being present. This latter view having support from the work of Fühner¹ who claims to have isolated four distinct substances from the posterior lobe of the pituitary gland, all of which give Pauly's reaction.

What compound or compounds we have to deal with here is suppositional at present, although evidence seems to be accumulating that points not to histidine but to some histidine-like compounds similar to histamine.² This view is also shared by Fühner³ who says: "According to the work of others and myself I am led to conclude that histamine and the active principle of the posterior lobe of the gland are probably not identical; but pharmacologically directly related."

Conclusions.

1. It would seem that histidine (or some such compound or compounds) is contained in the desiccated posterior lobe of the pituitary gland.
2. These substances are probably in a more or less free state, or in some combination other than protein.

¹ *Deutsche Med. Wochschr.*, 39, 491 (1913).

² Histamine is the commercial name for β -Iminazolyethylamine.

³ *Münch. Med. Wochschr.*, 599, 852 (1913).

3. The compounds giving Pauly's reaction are probably not histidine, since Weidel's reaction, as modified by Fischer, or Knoop's reaction with bromine were both negative.

4. Pauly's reaction is not a specific reaction for histidine, unless other compounds such as *l*-tryptophan, *o*-oxyphenylethylamine, β -iminazolyethylamine, etc., are excluded. The reaction for a class of compounds.

DETROIT, MICH.

[CONTRIBUTION FROM THE PHARMACOLOGICAL LABORATORY OF THE UNIVERSITY OF MINNESOTA.]

TRI-AMMONIUM CITRATE.

By ROBERT A. HALL.

Received November 20, 1914.

The ammonium salts of citric acid were seemingly first investigated by Heldt¹ in 1843, although in Berzelius' *Lehrbuch der Chemie* IV the statement is made that these compounds are very difficult to prepare and that no analysis of them had been made. Heldt's method of preparation was to neutralize a solution of citric acid with ammonia and by evaporation crystallize out the salts. His efforts to obtain the monoammonium citrate were unsuccessful, as his thick syrupy liquid always gave star-shaped groups of crystals containing varying amounts of ammonia. With the diammonium citrate he was more successful, as he obtained this salt in two separate, distinct crystalline forms. From a strong, concentrated solution after standing some hours, there separated out a mass of interlaced rhomboidal prisms; but upon slow evaporation in the cold winter air, the salt separated at the bottom of the vessel as a ring of massed oblique rhomboidal prisms with rectangular sides and semi-circular back-sides. In their composition both salts were identical and afforded a very interesting example of dimorphic organic compounds. Both crystalline forms rapidly absorbed moisture from the air and were soluble in boiling alcohol from which, upon cooling, they separated as oily drops. Their taste is agreeably acid with a cooling, bitter after effect. They were dried by pressing between filter paper and an elementary analysis made of their hydrogen and carbon content; the nitrogen was determined by precipitation as platinum ammonium hydrochloride. Both crystalline forms were found to have the composition represented by the formula $(\text{NH}_4)_2\text{C}_6\text{H}_6\text{O}_7$, that is, both were the diammonium citrate. Both salts were stable on heating to 100°.

Heldt's efforts at preparing the triammonium citrate were unsuccessful. He attempted to prepare this salt by evaporating a citric acid solution saturated with ammonia, but obtained the diammonium citrate. A

¹ Heldt, *Lieb. Ann.*, 47, 167 (—).

boiling alcoholic solution of citric acid, neutralized with ammonia, became cloudy upon cooling and deposited the salt as oily drops which did not crystallize even upon long standing.

Heusser,¹ in 1853, was evidently unacquainted with Heldt's earlier work on the ammonium citrates, for he says, "Concerning these salts (Citrates of Ammonium) I find nothing in the literature other than the observation in Berzelius's *Lehrbuch der Chemie* IV that they can be prepared unmixed only with great difficulty and no analyses thereof have been made." He attempted the preparation of the ammonium citrates but, in so far as the preparation of the triammonium citrate was concerned, he was no more successful than Heldt had been. He obtained the diammonium citrate and a compound that was probably a mixture of the di- and triammonium salts. His methods were essentially the same as those of Heldt.

F. Sestini,² in 1879, prepared a *neutral ammonium citrate* in crystalline form by neutralizing a solution of citric acid with ammonia and evaporating this solution over quick-lime in an atmosphere of ammonia. The crystals thus obtained were dried between filter paper and analyzed, the ammonia content and water of crystallization only being determined. The salt had approximately the composition represented by the formula $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7 + \text{H}_2\text{O}$, that is, the salt was triammonium citrate with one molecule of water of crystallization. The crystals were monoclinic and were very unstable, going over into the diammonium citrate upon being dried at 105–110°.

Van Itallie,³ in 1908, for the purpose of investigating the failure of calcium to produce a precipitate when added to an ammoniacal solution containing oxalate and citrate, repeated the preparation of triammonium citrate by Sestini's method and with the same results. He says, "The compound is not easy to purify for analysis, as is easily understood, because it is so hygroscopic and so easily dissociated." In his analysis he determined the citric acid and ammonia content of his salt, as well as the water of crystallization. He, too, obtained the triammonium citrate with one molecule of water. From the data obtained in his physical-chemical measurements, using Schreinemaker's "Reste-Methode" of plotting his curves, he demonstrated that the triammonium citrates containing one or more molecules of water must necessarily be unstable.

The writer first prepared the salt, normal triammonium citrate, in 1911, shortly after the completion of his investigations which were published in the papers, "The Physical Properties of Aqueous Solutions Containing Ammonia and Citric Acid"⁴ and the "Preparation of Neutral

¹ *Pogg. Ann.*, 88, 121 (1853).

² *Gazz. chim. ital.*, 9, 298 (1879).

³ *Z. anorg. Chem.*, 60, 358 (1908).

⁴ *THIS JOURNAL*, 33, 711 (1911).

Ammonium Citrate Solutions by the Conductivity Method."¹ The salt thus obtained reacted alkaline, although the analyses showed it to have the composition of normal triammonium citrate. As this was contradictory to all the literature then existing on the subject, it was deemed advisable to make further investigation. In the spring of 1912, further samples of the salt were made, analyzed, and certain physical and chemical properties were observed.² The method of preparation and general properties of the salt were reported, for record, at the meeting of the Academy of Science of St. Louis, April 21, 1913.³ An informal oral announcement of the preparation and properties of the salt was also made at the following May meeting of the St. Louis Section of the American Chemical Society. Publication was deferred, as it was desired to continue the investigation of the salt along the following lines: (1) As to its physical-chemical properties—it was deemed necessary to determine experimentally the concentration of the NH_3 and citric acid ions in both a dilute solution and in a solution of the concentration used in the fertilizer analysis; also, to ascertain by determinations of the ionization constants the proper indicator to be used in testing the neutrality of the so-called "neutral" ammonium citrate solutions. (2) The character and effect of the growth that so frequently occurs in so-called neutral solutions of ammonium citrate. (3) The pharmacological properties of the salt.

In the summer of 1913 the investigation of the physical chemical properties had scarcely been begun in the Kent Chemical Laboratory, University of Chicago, when Dr. Hildebrand's paper, "Some Applications of the Hydrogen Electrode in Analysis, Research, and Teaching"⁴ appeared. Hildebrand had anticipated a part of the investigation planned and had announced his intention of investigating and determining the proper indicator for concentrated solutions of neutral ammonium citrate, so this part of the research was abandoned. The recent appearance of his paper on "The Preparation of 'Neutral' Ammonium Citrate"⁵ enabled me to employ his results in the examination of the salt under investigation and to complete that part of it. Although the investigation of the growth formation in the solution and the pharmacological properties of the salt is still incomplete, yet the importance of the salt, to the fertilizer chemist in particular, is thought to be sufficient justification for publishing the results so far obtained.

Hantzsch,⁶ in 1902, found, in his investigations of the behavior of weak

J. Ind. Eng. Chem., 3, 559 (1911).

¹ I am indebted to Messrs. John T. Ragsdale, Jr., and H. W. Ramsey, my students, of St. Louis, for their assistance in making these preliminary analyses.

Transactions of the Academy of Science of St. Louis, 22, No. 6, 40 (1913).

THIS JOURNAL, 35, 847 (1913).

J. Ind. Eng. Chem., 6, 577 (1914).

Ber., 35, 226, 2724 (1902); 40, 3798 (1907).

acids and pseudo-acids towards ammonia, that, by passing perfectly dry ammonia gas into solutions of weak organic acids and pseudo-acids in perfectly anhydrous indifferent solvents as ether or benzol, the ammonium salts of these weak acids and pseudo-acids and tautomeric forms of chloroamids, nitro derivatives, etc., hitherto regarded as unstable because of the dissociating effect of water, could be prepared and obtained pure in quantity. If proper care were taken to keep every trace of water from the compound until it had been freed from the mother liquor and perfectly dried, then these bodies were unaffected by moisture and could be freely exposed to the air. This suggested to me that triammonium citrate could be prepared by passing dry ammonia gas into a solution of anhydrous citric acid in an inactive anhydrous solvent, as ether or alcohol. This could be done by dissolving the anhydrous citric acid (made anhydrous by carefully heating the acid, *in vacuo*, to its melting temperature and carefully maintaining this temperature until the water of crystallization was completely removed) in an anhydrous indifferent solvent and then passing through the solution in excess a stream of perfectly dry ammonia gas. Since the diammonium citrate is soluble in boiling alcohol,¹ absolute alcohol probably could preferably be used as the solvent and precipitation would not occur until the formation of the triammonium citrate began. Moreover, only the pure triammonium salt would be obtained if the solution were kept at the boiling point until the acid had been completely converted into the normal salt. The yield would be quantitative. The normal salt could be freed from its mother liquor by decantation and by repeated washings with the anhydrous solvent finally removing the last trace of the solvent by suction on the filter pump. The salt, being thus perfectly dried, should be stable; it could then be exposed to the moisture of the air without undergoing decomposition, etc. The solvent and washings could be freed from ammonia and recovered in the usual way, thus reducing the loss incurred in the preparation to that of the excess of ammonia gas used (and even this loss could be prevented, if desired, by recovery of the ammonia). Results obtained fully justified these conclusions.

Experimental.

Preparation of the Normal Triammonium Citrate Salt.—I. Citric acid was freed from its water of crystallization by heating it to 150°, the melting point of the acid. The temperature was not allowed to go much above this point as the acid is decomposed by a higher heat. The removal of the water of crystallization was facilitated by the use of the vacuum pump. A weighed amount of this water-free acid was placed in a round bottom flask whose mouth was sufficiently large to permit the use of a rubber stopper through which three tubes passed. One tube was

¹ Heldt, *Loc. cit.*

for the admission of the ammonia gas; this tube extended nearly to the bottom of the flask and was slightly bent outward to avoid coming in contact with the extended flanges of the stirrer when in motion. Through the center of the stopper passed the stirrer which was propelled by a motor of a size sufficient to preclude the probability of the stirrer stopping during the experiment. The third opening was for the entrance of the lower end of the reflux condenser tube, which served the double purpose of an exit tube for the excess of ammonia gas and also for the condensation and return into the flask of the alcohol used as solvent, thus preventing the loss of alcohol. The upper end of the condenser was connected with a tightly fitting tube which conducted the excess ammonia out of doors. The ammonia gas was obtained from a tank of liquid ammonia, or was prepared by allowing strong ammonia water to drop into a flask containing solid sodium hydroxide and ammonium chloride. In either case, for the purpose of completely drying the ammonia, the gas was first passed through a reflux condenser and then through several upright towers filled with sodium hydroxide sticks. Absolute alcohol, distilled over sodium, sufficient to dissolve completely the citric acid and also to cover completely the stirrer when in motion, was added and brought to the boiling temperature by heating on an electric bath. Ammonia gas was then slowly bubbled into the boiling solution which, throughout the course of the experiment, was vigorously stirred by the electrically propelled stirrer. For some few minutes, dependent upon the concentration of the acid solution and upon the rate of admission of the gas, no precipitation occurred. This was as expected and was probably due to the formation of the mono and diammonium citrates which are soluble in boiling alcohol.¹ As soon as the formation of the triammonium citrate began, precipitation occurred and continued until all the acid had been converted into triammonium citrate. When the precipitation was completed the heat was discontinued, but the ammonia gas was allowed to pass through the solution until the flask had become entirely cool. This served to prevent air bearing water vapor from entering the flask as the flask cooled. The supernatant liquid was decanted from the salt which was washed several times by decantation with absolute alcohol, until the washings were free from ammonia, the salt then being pressed dry on the Büchner funnel, using the thin rubber sheet cover with the suction pump as suggested by Cortner.² The salt was further pressed out on a clay plate, dried for an hour on a *dry* steam bath, and then placed in a desiccator over sulfuric acid for 24 hrs. The yield of triammonium citrate was quantitative. The alcohol used as solvent and washings was freed from ammonia and recovered in the usual

¹ Heldt, *Loc. cit.*

² THIS JOURNAL, 36, 1967 (1914).

way, thus making the only loss in the preparation that of the excess of ammonia used.

2. The method of preparation was varied by substituting for anhydrous citric acid purest citric acid, containing one molecule of water of crystallization. Otherwise the preparation was carried out as given above. A salt as pure and as stable as that obtained from the anhydrous acid was obtained. The yield, however, was only 85%, as much of the salt adhered to the sides of the flask.

3. Again the method of preparation was varied by omission of the use of the (electrically propelled) stirrer. The flask was shaken by hand from time to time. There was observed a tendency of the precipitate to clog and stick to the walls of the flask. The flask was tightly corked up and allowed to stand for a week. It was found that the salt obtained was the normal triammonium citrate. The yield was not over 75%.

4. Another variation in the method of preparation was introduced, the substitution of ordinary 95% alcohol for the absolute alcohol used above, the other conditions remaining as given in the first method of preparation. From 60 g. of anhydrous citric acid about 30 g. of the normal salt was obtained. As the mixture of the di- and triammonium citrates adhered closely to the walls of the flask, it was easy to separate the pure salt.¹

5. Dry ammonia gas was passed into a cold anhydrous alcoholic solution of citric acid; precipitation occurred at once. The precipitate was very viscid and adhered to the walls of the flask and to the tube admitting the ammonia when the flask was shaken. A small amount of the precipitate was removed and, after being freed from the mother liquor, was found to be acid to litmus. The salt thus separated out was either the mono- or diammonium citrate—probably a mixture of the two. It was very deliquescent and unstable.² The passage of the ammonia was continued for several hours. The contents of the flask became warm from the heat of the reaction. A small sample was then removed from the flask and found to react acid. The flask was tightly corked and set aside for a week. It was then found that the salt had an alkaline reaction to rosolic acid. The salt was washed and dried as given above and was found to be triammonium citrate. The yield was not good.

Other solvents of citric acid, as ether, acetone, etc., were substituted for alcohol but were found to be unsatisfactory in that the insolubility of the mono- and diammonium citrates in these solvents led to their pre-

¹ While it has not been put to the experimental test yet, it is very likely that the citric acid with its water of crystallization can be used in this method also.

² Investigation of the mono- and diammonium citrates is being continued in this laboratory.

precipitation along with the normal salt and thus gave mixtures instead of the pure salt.

Properties of Triammonium Citrate.—Triammonium citrate, prepared from a solution of the anhydrous citric acid in absolute alcohol or from a solution of the pure citric acid containing water of crystallization, is a beautiful white, crystalline salt. It is stable in so far that it can be exposed to the air for more than 24 hrs. without appreciable change, can be heated for an hour or more on a dry steam bath, or kept indefinitely in a desiccator over sulfuric acid. Upon prolonged heating on the steam bath or prolonged exposure to the air the salt loses ammonia and doubtless passes over into the diammonium citrate.¹ It is exceedingly soluble in water and can not be recrystallized from its water solution by evaporation. When a saturated water solution, cooled in a freezing mixture of ice and salt, is poured into absolute alcohol similarly cooled, a mass of long, fine crystals is obtained. The crystals were unstable and were not analyzed.¹ They are probably the triammonium citrate with one or more molecules of water of crystallization.² (It is hoped to take advantage of the winter cold of Minnesota to prepare and to isolate this salt in a pure form by carrying out the preparation altogether in the out door cold.) If a saturated water solution of triammonium citrate at room temperature is added to alcohol, oily drops are obtained but no crystals.¹ The water solution of triammonium citrate is alkaline to rosolic acid, thus fulfilling the prediction of Hildebrand.³ On exposure to the air a water solution of the salt loses ammonia and reacts acid.

Since the diammonium citrate is soluble in boiling alcohol, it is evident that the triammonium citrate salt that has become acid by loss of ammonia can be purified either by the removal of the diammonium citrate by extraction with boiling absolute alcohol or by passing through the finely powdered salts suspended in hot alcohol an excess of dry ammonia gas and working it up as in the original preparation.

Analyses.

The carbon, hydrogen and nitrogen content was determined by elementary analyses of a sample of the salt that had been dried in the steam oven for an hour and then dried further for some days over sulfuric acid in a desiccator.

I. 0.2501 g. of the salt gave: 0.1583 g. of H_2O and 0.2712 g. CO_2 ; calc. for $(NH_4)_3C_6H_5O_7$: H = 7.05, C = 29.61; found: 7.04 and 29.58.

II. 0.2115 g. of subst. gave 0.3660 g. of N; calc. for $(NH_4)_3C_6H_5O_7$: 17.28%; found: 17.30%.

III. Assuming that the salt was pure triammonium citrate an 0.1 N solution was made.

50 cc. of this solution = 0.4050 g. of the salt, gave on distillation with excess standard alkali 0.08513 g. of NH_3 . Calc. for $(NH_4)_3C_6H_5O_7$: 21.01%; found: 21.02.

¹ Heldt, *Loc. cit.*

² Van Itallie, *Ibid.*

³ Hildebrand, *Ibid.*

The excess of alkali in the distillation flask was determined and the citric acid content of the salt thus found. Calc. citric acid for $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$: 78.98%; found: 78.96.

For analysis and trial by a chemist in actual comparison with solutions used in the daily determination of phosphoric acid content of fertilizers, a sample of the salt analyzed above was sent to Dr. Paul Rudnick, Chicago. His report is given below:

"We made up a solution of ammonium citrate from the triammonium citrate which you sent us. The quantity received was a little more than sufficient for 500 cc. in all. Its reaction to azo-litmin, by the method described in my paper¹ 'On the Preparation of Neutral Ammonium Citrate,' was neutral. Analysis by a determination of both the NH_3 and citric acid content of the solution showed that the salt which you sent me must, therefore, have been 99.92% pure triammonium citrate. The specific gravity of this solution was 1.0898 at 20°. Accordingly, we added a sufficient amount of the salt to make the specific gravity 1.09 at 20°. The ratio between ammonia and citric acid was then that required by the Patten and Marti standard.²

"We then prepared a solution of neutral ammonium citrate from pure citric acid and ammonia and analyzed four different samples of fertilizers with each of the two solutions. The results obtained were as follows:

INSOLUBLE PHOSPHORIC ACID.

| | Solution triammonium citrate. Per cent. | Official neutral ammonium citrate solution. Per cent. |
|---|--|--|
| 10 and 5 | 0.74 | 0.71 |
| Acid phosphate | 0.10 | 0.10 |
| Complete fertilizer containing acid phosphate only.... | 2.29 | 2.27 |
| Complete fertilizer containing acid phosphate and bone..... | 4.55 | 4.58 |

"The concordance between these results is all that could be expected."

Dr. Rudnick's results corroborate fully those obtained in this and in other laboratories,³ the data of which it is unnecessary to give. The importance of this salt to the fertilizer chemist is manifest.⁴ His literature of recent years has been replete with easy, simple, and exact methods of preparing the "neutral ammonium citrate" solutions used in the determination of the insoluble phosphoric acid content of commercial fertilizers. While these valuable and interesting physical-chemical and analytical methods have in the main contributed somewhat to rendering more easy the preparation of this difficult solution, yet in no one method, or combination of these methods, has the solution of the problem been found. No two chemists have been able to prepare "neutral ammonium citrate solutions" that were in exact agreement one with the other as to their neutrality or their ammonia and citric acid content. It is hoped that the successful preparation of this salt, triammonium citrate, in a stable, workable form marks the beginning of the end of his troubles. It would

¹ Rudnick, *J. Ind. Eng. Chem.*, 5, 12, 998 (1913).

² Patten and Marti, *Ibid.*, 5, 567 (1913).

³ Grateful appreciation is hereby expressed to Dr. Rudnick and the others who have so kindly contributed to the success of this investigation.

seem so in view of the very evident fact that it is but necessary to weigh out, or add to water a sufficient amount of the salt to give the required specific gravity, and the solution is ready. The ease with which the solution can be prepared from the pure salt would preclude the necessity of making up large quantities of the solution so that deterioration by standing would be avoided. Uniformity in the results obtained in this very important analyses would thus be predicated upon uniformity of the ammonium citrate content of the solution. The difference in the hydrogen ion concentration of the normal and neutral solutions of ammonium citrate is so very slight¹ that the difference in the analytical results are negligible; and the ease and certainty of preparation of an accurate solution from the pure normal triammonium citrate salt would seem to predetermine the question in favor of the use of the triammonium citrate. Since, however, the neutral solution is prescribed legally as the solution to be used in the fertilizer analysis and since any change in the legal status would be dependent upon the report of chemists who have tried out the salt, this preliminary publication is made, although, as has been noted, the investigation of the triammonium citrate as contemplated and desired is still incomplete.

Summary.

Triammonium citrate can be obtained readily and easily as a stable compound by the passage of anhydrous ammonia gas into citric acid dissolved in an anhydrous solvent. The best solvent for this purpose is absolute alcohol heated to its boiling point. The yield of triammonium citrate is quantitative. Ninety-five per cent. alcohol may be used, but the yield is not quantitative.

The salt is a stable, crystalline substance. Analyses show it to have the composition represented by the formula $(\text{NH}_4)_3\text{C}_6\text{H}_5\text{O}_7$. It reacts alkaline to rosolic acid. It is exceedingly soluble in water and can not be recrystallized from its water solution. Precipitated, in the cold, from an aqueous solution by addition of alcohol an unstable crystalline form of the salt is obtained.

From practical tests in laboratories where daily analyses of fertilizers are made it has been shown that the salt lends itself readily to the making of solutions of 1.09 sp. gr. at 20°; that this solution of normal ammonium citrate gives, in parallel phosphoric acid determinations, results practically identical with the most carefully prepared "neutral" ammonium citrate solutions and can, therefore, well be substituted for the so-called neutral ammonium citrate solution.

MINNEAPOLIS, MINN.

¹ Hildebrand, *J. Ind. Eng. Chem.*, 6, 578 (July, 1914).

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL,
NEW YORK.]

STUDIES ON ENZYME ACTION. XII. THE ESTERASE AND LIPASE OF CASTOR BEANS.

By K. GEORGE FALK AND K. SUGIURA.

Received September 28, 1914.

In a former paper,¹ the results obtained in the extraction of a castor bean preparation by water and by solutions of different salts made it appear probable that substances showing different types of hydrolytic activity toward esters existed in castor beans. Greater activity, under certain fixed conditions, toward ethyl butyrate than toward triacetin was found associated with substances soluble in water, while greater activity toward triacetin than toward ethyl butyrate was found associated with a substance or with substances insoluble in water.

For the sake of a convenient terminology, the terms esterase and lipase will be used in this paper to represent these two types of hydrolytic action under certain definite conditions, esterase referring to the substance exhibiting the first action, lipase to the substance exhibiting the second. There is, however, no intention of establishing arbitrary differences between the two kinds of action. Undoubtedly the substance termed esterase hydrolyzes complex esters such as the fats, and the substance termed lipase hydrolyzes simple esters to a certain extent.

In this paper some experiments with the castor bean preparation on the activity toward triacetin in different salt solutions will be described; then the separation of the esterase and of a lipase from the castor bean preparation will be shown, together with a study of their hydrolytic actions under various conditions; and finally the analyses of the different preparations and the forms of combination of the nitrogen in them will be given.

In all of the tests of hydrolytic actions which are given in this paper, the procedure was the same as that described in preceding papers. When the action of a given preparation was measured on ethyl butyrate, one cc. of the neutral ester was added to the stated amount of solution or mixture, while if the action on triacetin was studied, 0.5 cc. of this ester, practically neutral in reaction, was used. The mixtures were placed in the incubator at 38–40° for 24 or 48 hrs. (or other time as stated) and then titrated with standard sodium hydroxide solution, approximately 0.1 *N*. At the same time, suitable blanks were run as usual and the final results, which alone are given here, give the corrected values for the acid formed from each ester, in terms of cc. of 0.1 *N* solution. The tests with ethyl butyrate are generally designated by Et Bu, with triacetin, by Triac.

The castor bean preparation used in these experiments was prepared

¹ IX paper of this series, *THIS JOURNAL*, 35, 1904 (1913).

from a new lot of cold pressed castor beans.¹ The shells were removed by hand, the kernels ground, extracted exhaustively with ether in a Soxhlet apparatus, dried in air and ground to pass through a 40 mesh sifter. Throughout this work, toluene was added to every solution and mixture, when extracting, filtering, or testing activities, to prevent bacterial growth.

A number of extraction experiments were carried out with the new preparation according to the method described in the IX Paper² with the former preparation.

The results showed, in agreement with the former work, that 70% of the material showing activity toward ethyl butyrate and 33% (50% in the former work) of the material showing activity toward triacetin, could be extracted by water.

Some tests of the activity of the preparation in sodium chloride and sodium sulfate solutions toward triacetin are of interest. With 0.2 g. castor bean preparation, 25 cc. solution, 0.5 cc. triacetin, and 24 hrs. tests, the following results were obtained:

TABLE I.—ACTION IN AQUEOUS SODIUM CHLORIDE AND SODIUM SULFATE SOLUTIONS OF CASTOR BEAN PREPARATION ON TRIACETIN.

| | 0. | 0.02 M. | 0.05 M. | 0.1 M. | 0.1 M. | 0.5 M. | 1 M. |
|---------------------------------------|------|---------|---------|--------|--------|--------|------|
| NaCl..... | 1.50 | 1.46 | 1.48 | 1.91 | 2.32 | 1.97 | 1.22 |
| Na ₂ SO ₄ | 1.55 | .. | .. | 3.51 | 4.32 | .. | .. |

In the V Paper of this series³ it was shown that sodium chloride inhibited the action toward ethyl butyrate, the effect being distinct even at 0.005 *M* and increasing with increase in concentration of the sodium chloride. Toward triacetin the activity increased with increasing salt concentration to a maximum at about 0.2 *M* and then decreased again. These results are strikingly similar to those obtained with duodenal contents.⁴ These showed in a series of tests with water and with 0.1 *M* sodium chloride solution that the presence of the salt inhibited markedly the action toward ethyl butyrate in every case, but that toward triacetin either very slight inhibition or marked acceleration was shown. The probable presence of an esterase and a lipase in intestinal contents under different conditions was described in the tenth paper. It would appear from these results, that the esterase and the lipase present are affected differently by the salts, the action of the esterase being inhibited by the simple uni-univalent salts at all concentrations, that of the lipase being accelerated at certain concentrations and inhibited at other, higher, concentrations.

¹ Supplied by the Baker Castor Oil Company, New York.

² *Loc. cit.*

³ THIS JOURNAL, 35, 601 (1913).

⁴ X paper of this series, THIS JOURNAL, 36, 1054 (1914). Cf. also the work of Terroine (*Biochem. Z.*, 23, 404 (1910)) with animal pancreatic juice.

Sodium sulfate exerted no apparent action on the activity of the castor bean preparation toward ethyl butyrate, but exerted marked acceleration toward triacetin. It is possible that here a retarding action of the sodium and accelerating action of the SO_4 on the two enzymes exert their influences to produce the results observed.

The effect of drying and of heat on the activity of the ether extracted, air dried castor bean preparation was studied. The preparation was placed in a vacuum desiccator containing calcium chloride or phosphorus pentoxide for the required lengths of time, the loss in weight determined and the activity of 0.18 g. portions tested toward ethyl butyrate and triacetin in 25 cc. H_2O for 24 hrs. at $38-40^\circ$. Other portions were heated and tested similarly, and finally some portions were first dried in desiccators, then heated, and finally tested. The results are given in Table II.

TABLE II.—ACTION OF DRYING AND OF HEAT ON THE LIPOLYTIC ACTIVITY OF THE CASTOR BEAN PREPARATION.

| Treatment. | Grams taken. | Loss. Gram. | Loss. Per cent. | Activity. | |
|--|--------------|-------------|-----------------|-----------|--------|
| | | | | Et Bu. | Triac. |
| CaCl_2 desiccator, 3 days..... | 1.0034 | 0.0719 | 7.17 | 1.59 | 1.56 |
| P_2O_5 desiccator, 2 days..... | 1.0074 | 0.1055 | 10.47 | .. | .. |
| 1 day more..... | .. | 0.1067 | 10.59 | 1.70 | 1.70 |
| $100-110^\circ$, 3 hrs..... | 1.0211 | 0.0930 | 9.11 | 0.31 | 0.61 |
| 100° , to constant weight..... | 2.5048 | 0.2573 | 10.27 | 0.68 | 0.95 |
| CaCl_2 desiccator, 2 days..... | 1.0299 | 0.0667 | 6.47 | .. | .. |
| 2 days more..... | .. | 0.0719 | 6.98 | .. | .. |
| Then $100-110^\circ$, 3 hrs..... | .. | 0.0988 | 9.59 | 0.13 | 0.41 |
| P_2O_5 desiccator, 3 days..... | 1.0033 | 0.1022 | 10.19 | .. | .. |
| Then $100-110^\circ$, 3 hrs..... | .. | 0.1038 | 10.34 | 0.28 | 0.64 |

The activity of the preparation did not decrease on drying in a vacuum desiccator over calcium chloride or phosphorus pentoxide. With the latter, considerably more moisture was taken out than with the former, as was to have been expected. On heating to $100-110^\circ$, although the loss in weight was not as great as in standing over phosphorus pentoxide, the activity was decreased very much. Also, first drying over calcium chloride to remove most of the moisture and then heating decreased the activity similarly. Drying over phosphorus pentoxide to remove practically all the moisture, and then heating, by which only 0.15% more was lost, decreased the activity just as much as if no preliminary drying had taken place. These results indicate that the inactivation due to heating the lipase is not connected with a simple loss of water or dehydration, but is doubtless due to some more deepseated chemical change.

The analysis of the castor bean preparation may be given here. The methods of analysis used were briefly as follows: Total ash was determined by careful heating and subsequent ignition of the material in a platinum dish, moistening with nitric acid and reignition until the ash

was no longer dark colored. The residue was taken up with water and nitric acid, calcium sulfate precipitated by sulfuric acid and alcohol, and, in the filtrate from this precipitate magnesium and phosphorus were determined in separate aliquot parts, each as magnesium pyrophosphate.¹ The analyses by the Neumann method were carried out by heating the material with concentrated sulfuric acid and addition of concentrated nitric acid until the mixture was colorless. After dilution, the calcium and magnesium were determined in the usual way, the phosphorus by precipitation with molybdate solution and weighing the precipitate $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ after drying at $110-120^\circ$ in a Gooch crucible.

Castor Bean Preparation.—9.70% moisture ($100-110^\circ$), 11.6% N (Kjeldahl), 6.70% ash, 4.13% P_2O_5 , 1.42% MgO, 0.16% CaO (Neumann method).

7.42% ash in dry substance.

13.9% N in ash- and moisture-free substance.

Esterase Material: Preparation and Properties.

In extracting the castor bean preparation with water it was found best to use a large number of small portions instead of few portions and large amounts of material. The extraction was more satisfactory in this method of working, more homogeneous mixtures were obtained and the filtration through asbestos was much more rapid. In the following work, which was carried on from the preparative standpoint, 0.5 g. preparation and 60 cc. water were used in each portion, and the extraction allowed to proceed for 24 hrs. since this length of time appeared to be sufficient to remove most, if not all, of the esterase. It was also found more convenient to centrifuge the extraction mixtures before filtering through asbestos, although this procedure was not essential.

The clear aqueous extracts contained the esterase or material with which the esterase was associated. 25 cc. of the extract required 0.20 cc. 0.1 N NaOH solution to be neutral toward phenolphthalein. Saturating the extract with $(\text{NH}_4)_2\text{SO}_4$ produced a flocculent precipitate, which, when dried on a porous plate, showed a small but appreciable activity, greater toward ethyl butyrate than toward triacetin under the standard conditions used. Owing to the presence of adsorbed ammonium sulfate, these titrations with alkali were carried out after the addition of neutralized formaldehyde solution. Precipitation of the aqueous extracts with other salts such as NaF, NaCl, MgSO_4 , or HgCl_2 gave either small amounts of inactive material or turbidities which could not be filtered. The addition of alcohol or of acetone to these solutions also produced marked turbidities from which, however, no solid material could be obtained either by centrifuging or by filtration.

Active solid preparations containing the esterase could be obtained by first dialyzing the clear aqueous extracts from the castor bean preparation

¹ Cf. Abderhalden, *Handbuch der bioch. Arbeitsmeth.*, 6 (1912).

before attempting precipitation. These clear extracts became very turbid on dialysis and small amounts of solid matter separated. At the same time they became very nearly neutral in reaction toward phenolphthalein. The volume of the solutions increased 8-10% on 24 hrs. dialysis against running water in collodion bags. The activity of the neutral turbid dialyzed solution was less than that of the slightly acid undialyzed extract, but the addition of the amount of acetic acid to the former necessary to produce the same acidity as the latter resulted in very nearly the same activity. The turbid dialyzed solutions could also be filtered and the clear solutions showed the same activity as the turbid. To obtain these clear filtrates, the turbid solutions must be passed repeatedly through hardened filter paper. The following tests of the activities of these solutions and mixtures may be cited in this connection:

Clear aqueous extracts.—Tested 25 cc. portions (acidity equivalent to 0.20 cc. 0.1 *N* NaOH), 24 hrs. Et Bu 1.23; Triac. 0.48.

Dialyzed this clear extract 18 hrs.—Very turbid. Tested 25 cc. portions (acidity equivalent to 0.08 cc. 0.1 *N* NaOH) after the addition of 0.12 cc. 0.1016 *N* acetic acid. Et Bu 1.06; Triac. 0.35.

Filtered the turbid dialyzed extract until clear.—Tested 25 cc. portions (acidity equivalent to 0.08 cc. 0.1 *N* NaOH) after the addition of 0.12 cc. 0.1016 *N* acetic acid. Et Bu 0.91; Triac. 0.18.

Clear aqueous extract.—Tested 25 cc. portions (acidity equivalent to 0.20 cc. 0.1 *N* NaOH), 24 hrs. Et Bu 1.05; Triac. 0.56.

Dialyzed 16 hrs., volume increased 8%.—Very turbid. Neutral. Tested 25 cc. portions. Et Bu 0.53; Triac. 0.25. Tested 30 cc. portions after addition of 0.20 cc. 0.1016 *N* acetic acid. Et Bu 0.96; Triac. 0.33.

Filtered dialyzed solutions till clear.—Tested 25 cc. portions. Et Bu 0.53; Triac. 0.24.

These results show clearly that the active esterase was contained in the clear neutral solution obtained after dialyzing and filtering the aqueous extracts of the castor bean preparation. The presence of small amounts of acid increased the activity of the esterase considerably, but its action was still very marked even without this added acid. The addition of dilute Ba(OH)₂ solution to the turbid dialyzed solution until it was strongly alkaline cleared up the turbidity to a great extent. This appears to eliminate any appreciable quantities of phytin as one of the constituents of the solution.

The effect of dialyzing the clear aqueous extracts of the castor bean preparation for different lengths of time was studied in so far as any action was noticeable on the activity of the solutions. In Table III, the first column indicates the lengths of time the clear extracts of the castor bean preparation were dialyzed in collodion bags against running water having a temperature between 10° and 15°. The second and third columns show the volumes of the solutions before and after dialysis. The fourth column gives the volumes of the solutions used in making the activity tests. These

tests were made after filtering the turbid dialyzed solutions. The last four columns give the results of the activity tests made directly without the addition of acid. Under "Found" are given the results actually obtained, under "Cor." are given the results calculated from those "Found," to 25 cc. of original undialyzed solution. These corrected results give a truer measure of comparative activities. The analyses of the solid preparations obtained from these solutions will be given in Table IV in connection with some other analyses.

TABLE III.—THE EFFECT OF DIALYSIS ON THE ACTIVITY OF THE ESTERASE.

| Time of dialysis. Hrs. | Volume. | | Cc. used for activity tests. | Activities, 24 hrs. | | | |
|---------------------------|-------------------------|------------------------|------------------------------|---------------------|------|--------|------|
| | Before dialysis. Cc. | After dialysis. Cc. | | Et Bu. | | Triac. | |
| | | | | Found. | Cor. | Found. | Cor. |
| 5 | 1150 | 1200 | 25 | 0.77 | 0.80 | 0.27 | 0.28 |
| 18 | 350 | 375 | 25 | 0.73 | 0.78 | 0.24 | 0.26 |
| 20 | 900 | 960 | 25 | 0.59 | 0.63 | 0.29 | 0.31 |
| 66 | 650 | 720 | 25 | 0.44 | 0.49 | 0.18 | 0.20 |
| 90 | 900 | 1000 | 25 | 0.34 | 0.38 | 0.12 | 0.13 |
| 93 | 800 | 840 | 25 | 0.33 | 0.35 | 0.23 | 0.24 |

These results show that the activity of the esterase decreased on continued dialysis, these decreases being very nearly proportional to the times of dialysis.

The turbid dialyzed solution precipitated with alcohol gave a solid preparation which showed no activity. Precipitation with three volumes of acetone, standing over night, filtering, grinding repeatedly with fresh acetone, and drying in a vacuum desiccator gave active preparations. Some tests with these preparations, called E_I for convenience, follow:

| | | | | | | | |
|---|------|------|------|------|------|------|--|
| 0.1 g. E_I , 50 cc. water, 0.50 cc. 0.1016 N acetic acid, 48 hours' test; Et Bu 1.40. | | | | | | | |
| 0.02 g. E_I , 50 cc. H_2O , 48 hours' test; different amounts 0.1016 N acetic acid. | | | | | | | |
| cc. 0.1016 N acetic acid..... | 0 | 0.10 | 0.20 | 0.30 | 0.40 | 0.50 | |
| Activity toward Et Bu..... | 0.10 | 0.20 | 0.18 | 0.19 | 0.18 | 0.14 | |

An esterase preparation, E_{II} , was prepared from the clear filtrate from the turbid dialyzed extract similarly by precipitation with acetone, filtering, grinding with fresh acetone and drying in a vacuum desiccator.

The activity of E_{II} is shown by the following result: 0.05 g. E_{II} , 25 cc. water, 0.20 cc. 0.1016 N acetic acid, 24 hours' test; Et Bu 0.53, Triac. 0.13.

In preparing E_{II} , it was found that, using apparently the same procedure and manipulation, at times solid material was obtained showing no activity. The reasons for these differences are entirely unknown.

Attempts to prepare purer material by dissolving E_I or E_{II} in water, filtering, dialyzing, filtering again, and precipitating with acetone gave solid preparations showing only small activity toward ethyl butyrate.

The castor bean preparation gave strong reactions for tyrosine (Folin's reagent¹), tryptophane (Hopkins-Cole test), aromatic group (Xantho-

¹ *J. Biol. Chem.*, **12**, 239 (1912).

proteic test) and carbohydrates (Molisch test). 5-10 mg. substance were used in these and the following tests. The esterase preparations E_I and E_{II} gave negative tests for carbohydrates, positive tests for tryptophane and aromatic groups, and very faintly positive for tyrosine. The redissolved and reprecipitated E_I preparation gave negative tests for tyrosine and tryptophane, otherwise no change.

The results obtained in determining moisture, ash, and P_2O_5 , in the different esterase preparations are given in Table IV.

TABLE IV.—ANALYSES OF ESTERASE PREPARATIONS.

| Preparation. | % loss in 3 hrs. at 100-110°. | % ni- trogen. | % ash. | % P_2O_5 . | % ash in dried subst. | % nitrogen in ash and moisture-free substance. |
|-----------------------------------|-------------------------------------|------------------|--------|--------------|-----------------------------|---|
| E_I | 8.55 | 12.8 | 8.03 | 3.85 | 8.78 | 14.4 |
| E_{II} (5 hrs. dialysis) | 6.56 | 13.9 | 4.80 | 2.08 | 5.14 | 15.7 |
| E_{II} (20 hrs. dialysis) | 8.38 | 14.2 | 4.26 | 1.43 | 4.65 | 16.3 |
| E_{II} (66 hrs. dialysis) | 7.52 | 14.0 | 4.70 | .. | 5.08 | 15.9 |
| E_{II} (90 hrs. dialysis) | 7.80 | 13.5 | 4.62 | 0.85 | 5.00 | 15.4 |
| E_I (reprecipitated) | 7.37 | 15.2 | 1.26 | 0.08 | 1.36 | 16.6 |

The amount of nitrogen in the esterase preparations was considerably greater than in the original castor bean preparation, while the percentage of ash was less, except for E_I . The percentage of nitrogen and the absence of carbohydrate reaction indicate that the preparation is mainly, if not entirely, protein in nature. The length of time of dialysis exerted no influence on the percentage of ash present, while with the nitrogen the differences in the different preparations showed no regularities and were probably accidental. The preparation E_I , obtained by precipitating the turbid dialyzed extract, contained more ash and less nitrogen than did the preparation E_{II} obtained by precipitating the clear filtered dialyzed extract. The reprecipitated preparation showed less ash and more nitrogen than did any of the others, but this preparation was only slightly active. The only regularity between the activity and the composition appeared to be in the percentage of P_2O_5 present. For the series E_{II} and times of dialysis and including the reprecipitated E_I , the greater the activity, the more P_2O_5 was present.

The existence of the water soluble esterase in castor beans is of interest in connection with some work on the hydrolysis of organic phosphorus compounds by enzymes published recently by R. H. A. Plimmer.¹ Plimmer found that the enzyme glycerophosphatase, capable of hydrolyzing glycerophosphoric acid into glycerin and phosphoric acid, was present in extracts of intestinal mucosa, kidney, castor oil seeds, yeast, and bran, but not in pancreas or liver extracts. He considered that "the absence of the enzyme from the extracts of pancreas and liver, which were prepared specially for lipase, and the presence of the enzymes in the extracts of the intestine

¹ *Biochem. J.*, 7, 43 (1913).

and kidney, tissues not usually regarded as good sources of lipase, point to this enzyme being distinct from lipase. Proof of the difference of the enzymes is given by the experiment with castor oil seeds; lipase is insoluble in water but an aqueous solution contains glycerophosphatase." As far as castor beans are concerned, the work described in this paper shows a soluble esterase to be present in them. In the course of this work, intestinal secretions and pancreatic juice and bile were tested for ester-splitting enzymes, and it is significant that it was made extremely probable in the X Paper that an esterase existed in intestinal juice and a lipase in pancreatic juice and bile. Although the evidence is not direct or complete, it is likely that the esterase and glycerophosphatase, if not identical, exist together and may be detected in preparations from the same sources.

Lipase Material: Preparation and Properties.

The residues of the castor bean preparation, after extracting with water, contained the greater part of the lipase, active toward triacetin. Evidence obtained in the extraction experiments indicated that the water-insoluble lipase was somewhat soluble in sodium chloride solutions.¹ Some preliminary experiments on the water-insoluble lipase material with different salt solutions showed that sodium chloride was the most satisfactory salt to use and the further experiments were, therefore, carried out exclusively with it.

A number of extraction experiments with sodium chloride solutions of different concentrations were made. The results are given in Table V. The water-soluble esterase was first removed by extraction as described. The residues from these extractions were then combined and treated with the requisite sodium chloride solution in the ratio of residues corresponding to one gram original castor bean preparation to 100 cc. salt solution. These were allowed to extract 24 hrs. at room temp., filtered clear through asbestos with suction, and the filtrates dialyzed 18 to 20 hrs. against running water in collodion bags. White precipitates formed in the solutions in the bags as the salt was removed by dialysis. The removal of the sodium chloride was almost always complete in 18 hrs. The volumes of the solutions increased as a rule. After dialysis, aliquot portions of the mixtures (solutions + precipitates) were tested for activity in the usual way. Practically no activity toward ethyl butyrate was found for any of the mixtures. With the triacetin tests, the activities found for the mixtures after dialysis were calculated for purposes of comparison to correspond to the amount of extracting solution obtained from the extraction of 0.2 g. original castor bean preparation.

A number of sets of such experiments were carried out. In place of giving the details of these, only the mean values for the different concen-

¹ IX paper of this series, *Loc. cit.*, p. 1913.

trations of salt solutions used will be given. The first row of Table V shows the concentration of salt solution; the second, the activity, multiplied by 100, toward triacetin of the dialyzed mixture corresponding to 0.2 g. castor bean preparation; and the third row the results taken from the smoothed curve obtained by plotting concentration of extracting salt solution against the observed activities of the mixtures, as given in the first and second rows.

TABLE V.—SUMMARY OF LIPASE EXTRACTION EXPERIMENTS WITH SODIUM CHLORIDE SOLUTIONS OF DIFFERENT CONCENTRATIONS.

| | | | | | | | | | |
|----------------------------|------|------|------|-----|-----|-----|-----|-----|-----------|
| Conc. NaCl, normality..... | 0 | 0.1 | 0.2 | 0.3 | 0.5 | 0.6 | 0.7 | 0.8 | 1.0 |
| Activity found..... | 0 | 14 | 17 | 23 | 24 | 34 | 29 | 31 | 39 |
| Activity from curve..... | 0 | 14 | 18 | 21 | 27 | 29 | 31 | 33 | 36 |
| Conc. NaCl, normality..... | 1.25 | 1.50 | 1.75 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | Saturated |
| Activity found..... | 37 | 40 | 39 | 37 | 37 | 32 | 31 | 22 | 14 |
| Activity from curve..... | 38 | 40 | 39 | 38 | 35 | 32 | 29 | 24 | 14 |

These results show that 1.5 *N* NaCl solution extracted more active lipase than did any other concentration. In every salt extraction the removal of the salt by dialysis produced a precipitate in the solution. These mixtures, the activities of which were given in Table V, could be filtered readily. The filtrates showed no activity toward triacetin. The solid material must, therefore, contain the active lipase.

In the further work with this lipase, two extracting solutions were used; a saturated salt solution, giving the largest quantity of solid, the material obtained being designated *L*_I; and a 1.5 *N* salt solution, giving the most active extract, the material thus obtained being designated *L*_{II}.

The castor bean residues after water and repeated salt extractions still showed marked activity toward triacetin, but very little toward ethyl butyrate. The continued treatment of the castor bean preparation with water and especially with salt solution undoubtedly modified the properties of some of the substances, colloidal and other, present originally in the preparation. The fact that the residues after the extractions described still show such marked activity, indicates that one or more other lipases are present which could not be obtained by the simple extractions described.

The effect of varying the times of dialysis of the salt extractions on the activity of the resulting mixtures was studied.

It was found that the activity of the lipase mixture was not diminished appreciably even after dialyzing continuously for six days. This behavior was in marked contrast to that of the esterase, the activity of which diminished fairly rapidly on continued dialysis. The difference in physical properties may account in part for this; the esterase remained in solution, while the lipase was precipitated out as the salt was removed and remained suspended in the solution.

A number of attempts made to obtain the solid enzyme L_I in active form from the dialyzed mixtures of the saturated salt solution failed.

More extended experiments were made with the L_{II} mixture as obtained by dialyzing the 1.5 N salt extractions. First the activity of mixtures in water and in the salt solutions, suspended and dissolved, were compared. 800 cc. of 1.5 N salt extract were divided into two parts. 400 cc. were dialyzed for 48 hrs. against running water. The salt was removed completely and the volume increased to 565 cc. 50 cc. tested for 24 hrs. gave an activity of 0.62 toward triacetin. The remaining 400 cc. of the extract were allowed to stand at room temperature 48 hrs., the volume brought to 565 cc. with 1.5 N salt solution, 50 cc. portions tested for 24 hrs., giving an activity of 0.56 toward triacetin. Whether the material was dissolved in the salt solution or suspended in the aqueous solution appeared to be of small influence on its hydrolyzing action.

The L_{II} solution mixture after being dialyzed, filtered, the residue washed thoroughly with water, and taken up with fresh water, showed very marked lipolytic action, indicating that the dialyzed solution contained no essential constituent (such as a coenzyme) of the lipase, but that the activity was all concentrated in the solid material L_{II} .

A number of tests with 50 cc. L_{II} water mixtures, 24 hrs., with added salts were made:

| | H ₂ O. | 0.1 M NaCl. | 0.05 M NaF. | 0.05 M MgSO ₄ . | 0.002 M MnSO ₄ . |
|---------------------|-------------------|---------------|---------------|------------------------------|-------------------------------|
| Rt Bu activity.... | 0.11 | 0.09 | 0.08 | 0.10 | 0.09 |
| Triac. activity.... | 0.92 | 0.95 | 0.48 | 0.89 | 0.97 |

The only marked influence of the salts was shown by the sodium fluoride, which inhibited the action strongly. The lack of either retarding or accelerating action of the sodium chloride is of interest, as well as the lack of accelerating action of the magnesium sulfate. Series of experiments in which the amount of water and the amount of triacetin were varied were also carried out. In the following experiments, different quantities of the L_{II} -water mixture and water were tested with 0.5 cc. triacetin for 24 hrs.:

| | | | | | | | |
|----------------------------------|------|------|------|------|------|------|------|
| Cc. L_{II} -water mixture..... | 10 | 20 | 40 | 60 | 10 | 10 | 10 |
| Cc. water added..... | 0 | 0 | 0 | 0 | 10 | 30 | 50 |
| Activity..... | 0.40 | 0.90 | 1.59 | 1.97 | 0.41 | 0.37 | 0.30 |

Except for the largest amount of L_{II} -water mixture used, the action was approximately proportional to the quantity of the L_{II} present. Similarly for the same amount of L_{II} -water mixture, addition of water exerted no influence on the reaction except for the largest quantity of water added.

With 50 cc. L_{II} -water mixture and different amounts of triacetin, 24 hrs. tests gave the following results:

| | | | | | | | | |
|--------------------|------|------|------|------|------|------|------|------|
| Cc. triacetin..... | 0.1 | 0.2 | 0.3 | 0.5 | 0.8 | 1.0 | 1.5 | 2.0 |
| Activity..... | 0.46 | 0.59 | 0.66 | 0.73 | 0.75 | 0.77 | 0.73 | 0.77 |

After a certain amount of triacetin, addition of still more did not increase the amount of action with the given quantity of lipase. The results of the last two series indicate that a definite quantity of lipase can only react with a certain quantity of triacetin in a given time. 0.5 cc. triacetin is the maximum amount with which 50 cc. L_{II} -mixture could react, so that the result with 60 cc. L_{II} -mixture in the previous series was not proportional to the less amounts of lipase, because in the latter case an excess of triacetin was present, in the former, insufficient triacetin.

The precipitated L_{II} in the mixtures was readily dissolved by small amounts of dilute hydrochloric acid, sodium hydroxide, or glacial acetic acid, but not dilute acetic acid.

The solid L_{II} material was prepared by filtering the precipitate from the dialyzed solutions on hardened paper, grinding with acetone in a mortar for some time and finally drying in a vacuum desiccator. The white powder obtained in this way was, however, only slightly active. The addition of small amounts of acetic acid or of sodium hydroxide did not increase the activity. This behavior is in marked contrast to that of the esterase which could be obtained active in solid form readily.

An attempt was made to obtain a more homogeneous material from the L_{II} , if possible. Two grams of L_{II} were treated with 100 cc. 1.5 *N* sodium chloride solution. After ten minutes, when most of the solid had gone into solution, the mixture was filtered through hardened paper, the opalescent filtrate dialyzed against running water 20 hrs., a heavy white precipitate forming and the volume increasing to 300 cc. Practically no activity was shown by the mixture.

The analyses of the lipase preparations are given in Table VI.

TABLE VI.—ANALYSES OF LIPASE PREPARATIONS.

| Preparation. | % Loss in 3 hrs. at 100–110°. | % Ni- trogen. | % Ash. | % P_2O_5 . | % Ash in dried subst. | % Nitrogen in ash and mois- ture-free substance. |
|-----------------------------------|-------------------------------------|------------------|--------|--------------|-----------------------------|--|
| L_I | 9.76 | 14.3 | 6.29 | 3.93 | 6.95 | 17.0 |
| L_{II} (24 hrs. dialysis)..... | 6.57 | 15.1 | 4.04 | .50 | 4.32 | 16.9 |
| L_{II} (44 hrs. dialysis)..... | 5.37 | 15.3 | 3.96 | .54 | 4.19 | 16.9 |
| L_{II} (67 hrs. dialysis)..... | 6.96 | 15.0 | 3.89 | .76 | 4.18 | 16.8 |
| L_{II} (92 hrs. dialysis)..... | 8.26 | 14.1 | 5.71 | .77 | 6.22 | 16.4 |
| L_{II} (115 hrs. dialysis)..... | 8.00 | 14.5 | 4.80 | .85 | 5.22 | 16.6 |
| L_{II} (141 hrs. dialysis)..... | 7.00 | 15.1 | 3.60 | .14 | 3.87 | 16.9 |
| L_{II} (reprecipitated)..... | 7.59 | 16.1 | 0.70 | 0.20 | 0.76 | 17.6 |

The length of time of dialysis exerted no effect on the composition of the lipase preparation. The percentage of ash varied irregularly and is doubtless due to accidental causes. The only distinct features of the analyses are the facts that L_I , obtained with saturated salt solution, con-

tained most ash, and that the redissolved and reprecipitated L_{II} preparation contained less ash and more nitrogen than any of the other preparations.

Both the L_I and L_{II} preparations gave negative tests for carbohydrates (Molisch test) faintly positive for tyrosine (Folin reagent), distinctly positive for tryptophane (Hopkins-Cole test) and strongly positive for aromatic groups (Xanthoproteic test).

A characteristic property of the esterase of castor beans is its solubility in water, and of the lipase, its insolubility in water and solubility in salt solution. The hydrolytic power of these enzymes is doubtless associated with certain groups in the (presumably) protein molecule, and it is readily conceivable that these same groups might be present in protein molecules showing solubilities different than those of the castor bean preparation. It will be shown in a future paper, that the lipase of soy beans, which shows chemical properties similar in many respects to those of the lipase of castor beans, can be obtained dissolved in clear aqueous solution.

Chemical Nature of Preparations.

The principal forms in which nitrogen was present in the different preparations described in this paper were determined by Van Slyke's method.¹ The microapparatus² was used. About one gram of substance was hydrolyzed in each analysis. The final results are given in Table VII. The first set of results is for the castor bean preparation, the second for the esterase preparation E_I , the third for the lipase preparation L_I , the fourth for the lipase preparation L_{II} .

TABLE VII.—FORMS OF NITROGEN IN PREPARATIONS EXPRESSED AS PERCENTAGES OF TOTAL NITROGEN.

| | Castor bean preparation. | Esterase E_I . | Lipase L_I . | Lipase L_{II} . |
|-------------------------------------|-----------------------------|---------------------|-------------------|----------------------|
| Ammonia nitrogen..... | 12.1 | 12.2 | 10.0 | 10.5 |
| Melanine nitrogen..... | 3.3 | 1.5 | 1.7 | 1.8 |
| Cystine nitrogen..... | 3.1 | 2.9 | 2.6 | 2.6 |
| Arginine nitrogen..... | 24.7 | 24.1 | 27.1 | 24.9 |
| Histidine nitrogen..... | 6.2 | 4.4 | 6.5 | 4.9 |
| Lysine nitrogen..... | 4.3 | 3.7 | 2.3 | 3.9 |
| Amino nitrogen of filtrate..... | 49.4 | 49.0 | 53.6 | 51.8 |
| Non-amino nitrogen of filtrate..... | ... | 3.9 | ... | 1.5 |
| Totals..... | 103.1 | 101.7 | 103.8 | 101.9 |

In carrying out the hydrolyses by heating with 20% hydrochloric acid as recommended by Van Slyke, it was observed that with the solid preparations, the substances were charred rapidly and separated considerable quantities of black carbonized material. An analysis was, therefore,

¹ *J. Biol. Chem.*, **10**, 15 (1911); **12**, 275 (1912).

² *Ibid.*, **16**, 121 (1913).

made of an L_{II} -water mixture which had shown marked lipolytic action. Heating this mixture with the hydrochloric acid in the customary way resulted in a gradual darkening of the solution and deposition of very little black material. The results of this analysis are given in the column headed Lipase L_{II} . The preparation of the solid L_{II} from the L_{II} mixture involved treatment with acetone and was accompanied by the inactivation of the material. It is possible that some chemical change was brought about in this treatment which manifested itself in the different behavior of the preparations on treating with hydrochloric acid, although no clew as to the nature of this change is evident at present.

Very little difference is shown in the relative proportions of the forms of nitrogen in the castor bean, esterase and lipase preparations. The nitrogen content of the ash-free esterase preparation E_{II} (15.4 to 16.3%) and of the ash-free lipase preparation L_{II} (16.4 to 16.9%) indicate that these consisted mainly, if not entirely, of protein material. The nitrogen distribution results confirm this conclusion in so far as it is shown that the forms in which the nitrogen exists in them are the same as those in which the nitrogen exists in other typical proteins, with differences in the amounts present in the different forms. The absence of carbohydrate substances (negative Molisch test), and of fats (method of preparation), also bears out the view that the preparations are essentially protein.

Sherman and Gettler¹ have furnished fairly conclusive proof that their amylase preparations, obtained in a high state of purity and in very active form, were essentially protein in character. Every enzyme must naturally be considered independently as far as its chemical constitution is concerned, but it is a significant fact that up to the present time, protein material has been found in every enzyme preparation which has been investigated carefully and purified as far as possible. The amounts of protein found vary greatly. The invertase preparations of Nelson and Born,² which appear to represent the products of greatest purity for this enzyme obtained up to the present, showed an average nitrogen content of about 1.3%, while at the other extreme are the amylase preparations of Sherman and Gettler and the esterase and lipase preparations described here which appear to be entirely protein in character.

In considering whether the protein itself, or some part of it, can produce reactions which are characteristic of enzymes, it has been found possible to go somewhat further with the lipolytic actions than with the actions caused by other enzymes. Work in this laboratory has shown³ that simple aminoacids not only exert hydrolytic actions on esters, but that relatively

¹ THIS JOURNAL, 36, 1790 (1913).

² *Ibid.*, 36, 396 (1914).

³ II paper of this series, THIS JOURNAL, 34, 828 (1912); M. L. Hamlin, VII and VIII Papers, *Ibid.*, 35, 624, 1897 (1913).

simple differences in the structures of aminoacids caused changes in the rates of hydrolyses of simple esters not dependent upon the hydrogen ion concentration alone; in other words, that they act selectively on the esters. These actions, it is true, are comparatively small, but, if simple aminoacids can be shown to duplicate, even to less degree, the actions of different lipases, it is not only possible, but probable, that groupings in complex proteins exist and may be found which will account for the enzymatic changes. There is no direct evidence that such groupings are the active factors, but the indirect evidence shows that the existence of such groupings is probable and would be sufficient to account for the reactions.

The writers wish to thank Mr. Morris Erenstoft for his efficient aid in carrying out the experimental work described in this paper.

Summary.

The extraction results described in a former paper were confirmed with a new castor bean preparation.

The action of the castor bean preparation on triacetin in the presence of some neutral salts was described. The activity of the preparation was tested after drying and heating under different conditions.

An esterase preparation, active toward ethyl butyrate, was separated by extraction with water, and its properties studied in solution and in the solid form. Its probable identity with glycerophosphatase was suggested.

A lipase preparation, active toward triacetin, was separated by extraction with 1.5 *N* sodium chloride solution, and its properties studied.

The forms of combination of the nitrogen in the preparations were determined. The probable protein nature of the esterase and lipase was discussed.

NEW YORK, N. Y.

THE TOTAL AMINO NITROGEN IN THE SEEDLINGS OF THE ALASKA PEA.

By THOS. G. THOMPSON.¹

Received October 24, 1914.

While considerable attention appears to have been devoted to the occurrence of asparagin in plants, very little study seems to have been given to the total amount of amino and amide nitrogen that exists in plants at various stages of growth. Schulze² published his ideas concerning the formation of amino acids in plants in 1898. Later Scruti³ pointed out the importance played by phosphorus in the formation of acid amides and amino acids which go to build up the protein molecules. It is a gener-

¹ Acknowledgment is made to Dr. G. F. White who suggested and supervised this research.

² *Z. chim. Physiol.*, 24, 1898.

³ *Staz. sper. agrag. Ital.*, 41, 456.

ally accepted fact that the existence of these nitrogenous compounds is a result both of the decomposition of the plant proteins and of synthetic processes. The exact steps of the syntheses are not definitely known. Franzen¹ has worked out a long series of reactions explaining, from a purely theoretical standpoint, the synthetic formation of the amino acids and the acid amides. His assumptions are based entirely upon the theory of Treub, in that the formaldehyde unites with the ammonia and the hydrocyanic acid to form the amino nitriles, which are later subjected to hydrolysis. The formaldehyde is formed by the reduction of the carbonic acid, and the ammonia and hydrocyanic acid are considered as the reduction products of the nitrates. From the theoretical explanation of Franzen and the experimental work of several investigators, it is concluded that the nitrogenous matter in the plants is constantly undergoing changes. Thus the percentage of the amino nitrogen should vary at different stages in the growth of the plant.

In 1890, Frank called attention to the fact that the leaves of plants contain more asparagin in the evening than in the morning. Kiesel² much later made a study of the changes undergone by the nitrogenous matter in *Trifolium Pratense Rept.* When the plants were kept in the dark he was able to demonstrate the presence of a small amount of arginine and showed the absence of other hexone bases. In the fresh plants, those that had been influenced by the action of sunlight, he was able to detect slight traces of amino valeric acid and leucine with more or less certainty. Upon keeping the plants in the dark for some time, however, enough leucine was present so that it was identified without any difficulty.

Andre³ studied the percentage of amino and amide nitrogen in the nitrogenous materials found in the leaves of plants at different stages of their growth during the year. The leaves in active life, during the months from May to October, upon subjection to analysis, indicated that the total nitrogen (dry material) decreased from 3.4% to 1.8%, while the amino nitrogen at first decreased from 0.53% in May to 0.10% in July, and then gradually increased again to 0.48% in October. As the result of his work, he concludes that the elaboration of the amide nitrogen may be considered uniform throughout the life of the leaf, with the exception of the period of fertilization of the flowers. At this period, translocation of the nitrogenous matter in the plant became very marked.

Experimental.

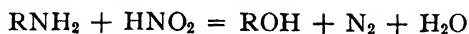
This investigation was undertaken to obtain some systematic data concerning the relation of the total nitrogen to the amino nitrogen in the grow-

¹ *Chem. Zentr.*, 1910, II, 983.

² *Z. physiol. Chem.*, 49, 72-80 (1906).

³ *Compt. rend.*, 148, 1685-1687.

ing plant, applying a method for the determination of the amino nitrogen which would prove to be, at the same time, both accurate and simple. The method used in the determination of the amino nitrogen in this research consists in the measurement of the nitrogen evolved according to the general reaction:



This reaction was permitted to take place in the apparatus recommended and fully described by D. D. Van Slyke¹ for the determination of small percentages of amino nitrogen. This apparatus was utilized exclusively in obtaining the percentages given below. In brief, it consists of a deaminizing vessel which is connected with a buret of 2 cc. capacity and a tube through which acetic acid and sodium nitrite are permitted to flow into the deaminizing vessel. A small buret is used to introduce the required amount of sample, containing the amino acids, into contact with the solution of the nitrous acid. The deaminizing portion of the apparatus is also connected to a gas buret that is graduated to 0.02 cc. This in turn is joined to a Hempel pipet containing an alkaline solution of potassium permanganate for the absorption of the nitric oxide, which is liberated in considerable quantities during the reaction. The detailed manipulation of the apparatus is completely described by Van Slyke in both of his papers. The modified form of the apparatus was used in making all the analyses reported in this paper.

For the purpose of determining the total nitrogen present in the seedlings, the standard Kjeldahl method was utilized.

In running blank determinations with the amino apparatus, a small volume of gas that was not absorbed by the alkaline potassium permanganate was obtained on using sodium nitrite that had been permitted to stand for a day and then filtered from the slight amount of sediment. After running a number of blank determinations and securing their readings it was found that a correction of 0.188 mg. of nitrogen would have to be made. On the other hand, if sodium nitrite was employed that had not been filtered, it was found that a greater amount of gas remained unabsorbed, and thus a correction of 0.199 mg. of nitrogen would be necessary in the regular determinations. In all the experimental work given in this paper, only the filtered sodium nitrite was employed.

From one and a half to five grams of the samples of the seedlings, or different portions of the plant for analysis, were weighed out, transferred and ground finely in a mortar. Water was then added to dissolve the amino acids that were present. As some of the proteins are more or less soluble in water, a drop of glacial acetic acid was introduced into the solution in order to precipitate those that might be present. The solutions were made up in graduated flasks of 25 cc., 50 cc., or 100 cc. capacity,

¹ *J. Biochem.*, 9, 185 (1911); 12, 275-284 (1912).

depending upon the size of the sample taken for analysis. Before running into the small buret, attached to the deaminizing vessel, the solutions were carefully filtered.

The formation and distribution of the amino acids and the acid amides in the Alaska pea were studied, special attention being given to its occurrence in the very young plants or seedlings. All the specimens for analysis were grown in a rich, moist soil and in a room of moderate temperature with full advantages for securing the rays of the sun. Every twenty-four hours a few of the seedlings were removed from the soil and, after removing all the earthy particles carefully with the aid of a soft brush, subjected to analysis. This was done for seven consecutive days with the following results:

TABLE I.

| | Natural. | | Dry material | | Amino N, Total N Per cent. |
|----------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|----------------------------------|
| | Total nitrogen. Per cent. | Amino nitrogen. Per cent. | Total nitrogen. Per cent. | Amino nitrogen. Per cent. | |
| 1-Day seedlings..... | 1.75 | 0.115 | 3.27 | 0.215 | 6.58 |
| 2-Day seedlings..... | 1.51 | 0.124 | 3.22 | 0.265 | 8.23 |
| 3-Day seedlings..... | 1.47 | 0.151 | 3.28 | 0.337 | 10.52 |
| 4-Day seedlings..... | 1.42 | 0.164 | 3.35 | 0.386 | 11.52 |
| 5-Day seedlings..... | 1.067 | 0.197 | 3.44 | 0.635 | 18.46 |
| 6-Day seedlings..... | 0.997 | 0.214 | 3.48 | 0.747 | 21.46 |
| 7-Day seedlings..... | 0.934 | 0.262 | 3.53 | 0.998 | 28.27 |

The original seed contained 0.088% of amino nitrogen.

In all cases, samples of the fresh plant were used for the exact estimation of both the total and the amino nitrogen. A third sample, for the determination of moisture, was always weighed out and dried in a closet at the temperature of boiling water for five or six hours. From the results given above, it is seen that there is a steady increase in the percentage of the amino nitrogen and that there is a marked increase in the occurrence of the amino nitrogen in the first- and the fifth-day seedlings. This increase in the first-day seedling is due, undoubtedly, to the decomposition of the proteins present in the original seed and indicates the formation of the food supply for the new protein material. The one-, two- and three-day seedlings all maintained the shape of the seed, but were, of course, much larger in size. The four-day seedling contained a small plumule, while the five-day seedling took the form of a regular plant. The plumules and roots of the six- and seven-day seedlings were larger and showed more signs of development. The large increase in the percentage of amino nitrogen in the five-day plant is probably explained by the rapid transformation of the seed and thus the requirement for a greater quantity of plant food of this nature to build up the highly elaborated nitrogenous material in the leaves, stems and roots. As the amino nitrogen increases at a much greater rate than the total nitrogen, there

must necessarily be a marked breaking down and decomposition of the proteins present in the original seed. This fact is also further emphasized in that there is a decided increase of amino nitrogen when expressed as the percentage of total nitrogen.

From the figures given in the foregoing table, it is seen that when the percentage of the total nitrogen decreases as indicated by the results obtained from the seedlings in their natural condition, the percentage of amino nitrogen increases. When this data is expressed in terms of dry material there is a slight increase in the total nitrogen and a very decided increase in the amino nitrogen.

In the case of the seven-day seedlings, the plumules, cotyledons and roots were analyzed separately and the following results were obtained:

TABLE II.

| | Natural. | | Dry material. | | Amino nitro. Total nitro. Per cent. |
|----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---|
| | Total nitrogen. Per cent. | Amino nitrogen. Per cent. | Total nitrogen. Per cent. | Amino nitrogen. Per cent. | |
| Plumule..... | 0.832 | 0.301 | 7.021 | 2.540 | 36.18 |
| Cotyledon..... | 1.534 | 0.202 | 3.36 | 0.421 | 12.53 |
| Root..... | ... | ... | 5.33 | 1.705 | 31.99 |

From the above it is seen that the plumule contains a much greater amount of amino nitrogen, which undoubtedly serves as a food supply for the newly forming leaves and stems. It was expected that the cotyledon would show a greater percentage of amino nitrogen, owing to the decomposition of the protein material that it contained. However, this was not the case, and it is probable that any amino acids that are formed there are translocated to the roots and the stems. This is further indicated by the fact that the percentages of the amino nitrogen in the plumule and the root are much greater than in the cotyledon.

The leaves, the stems near the top, and those near the roots of the plant, were subjected to analysis in the fourteen-, twenty-one and thirty-eight-day plant with the following results:

TABLE III.

| | Natural. | | Dry material. | | Amino nitro. Total nitro. Per cent. |
|-------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---|
| | Total nitrogen. Per cent. | Amino nitrogen. Per cent. | Total nitrogen. Per cent. | Amino nitrogen. Per cent. | |
| 14-Day leaves..... | 1.52 | 0.297 | 9.43 | 1.830 | 19.41 |
| 21-Day leaves..... | 1.52 | 0.244 | 9.29 | 1.495 | 16.09 |
| 38-Day leaves..... | 1.46 | 0.209 | 8.35 | 1.195 | 14.32 |
| 14-Day stem (top)..... | 0.745 | 0.303 | 7.801 | 3.173 | 40.67 |
| 21-Day stem (top)..... | ... | 0.283 | ... | 2.975 | ... |
| 38-Day stem (top)..... | 0.807 | 0.226 | 8.54 | 2.390 | 27.99 |
| 14-Day stem (root)..... | 0.693 | 0.300 | 8.59 | 3.717 | 43.30 |
| 21-Day stem (root)..... | 0.688 | 0.275 | 8.75 | 3.500 | 40.00 |
| 38-Day stem (root)..... | 0.675 | 0.187 | 8.54 | 2.364 | 27.68 |

The total nitrogen remains fairly constant in the natural leaves, but there is a noticeable decrease in the amino nitrogen. When these results are expressed in terms of the dry material, it is seen that there is a decrease in both the total and amino nitrogen as the plant increases in age. The same may be said of the stems both near the top and the bottom of the plant. It is also noticed that the amino nitrogen in the stems near the lower part of the plant are just a little less in percentage than the sample taken near the leaves.

In the case of these older plants it was impossible to get good, reliable results from the analysis of the roots because of the great difficulty of cleaning and freeing them from foreign materials. The results that were actually obtained from the analysis of the roots seemed to indicate a smaller percentage of amino nitrogen than was obtained in the stems. It also seems probable that the extreme ends of the roots contained a much smaller amount of amino nitrogen than the upper of the root.

CLARK COLLEGE, WORCESTER, MASS.

NEW BOOKS.

Landolt-Börnstein Physikalisch-Chemische Tabellen. Fourth edition, revised and enlarged. Prepared under the direction of DR. RICHARD BÖRNSTEIN AND DR. WALTHER A. ROTH. Berlin: Julius Springer. 1912. pp. xvi + 1310. Price, M. 59.

The greatest shortcoming of the previous editions of this indispensable work has been the entire lack of tables of certain important and much used data. The removal of this deficiency is responsible for the greater part of the increase in size of this edition over the previous one. Among the new tables the following may be mentioned: Homogeneous Gas Equilibria, Equilibria between Organic Substances, Distribution Coefficients, Ionization Constants, Conductivity Data for Non-aqueous Solutions, Hydrolysis Data, Radioactive Constants, and an extended table giving the chief physical properties of all of the more important organic compounds.

E. W. WASHBURN.

Notes on Elementary Inorganic Chemistry. By F. H. JEFFERY. Cambridge University Press. G. P. Putnam's Sons: New York. i + 55 pp. Price, 60 cents.

The purpose of the author of this small volume has been to present "short summaries of certain facts and reactions which are commonly included in a course on elementary inorganic chemistry." It is intended that the book be used in connection with lecture and laboratory work in order that the notes presented may "serve for revision purposes" and also that they may "afford the comparative beginner groups of facts which he might find difficult to coördinate for himself." Among the ten chapter headings are found such topics as: Acids, Bases and Salts, Oxidation and Reduction, The Action of Certain Acids on Some Metals, and Certain

Examples of Electrolysis. The author has brought together in small compass many of the facts in reference to the elements and compounds which are usually discussed in the beginning courses in our colleges and

the beginner in the science would have been greatly aided in the coördination of the facts of chemistry and some little use has been made of such useful instruments as the Periodic Law and also of some of the more commonly accepted theories. The almost entire absence of the terminology of these theories save in the chapter on "Certain Examples of Electrolysis" would seem to be unfortunate for the student. Some of the notions in reference to chemical equilibrium could have been introduced with great benefit in the chapter on "The Preparation of Certain Salts." Again, in the chapter on "The Action of Acids on Some Metals," a good opportunity is offered to present the electromotive series of metals as a useful aid in the work.

For the sake of clearness in the chapter on "Certain Examples of Electrolysis," it would have been better to represent the electrical charge carried by the cation and anion by different symbols rather than to use the same designation for both. Would not the student attach too great importance to potassium hydroxide by the first sentence on page 1; *viz.*, "The acids are compounds of hydrogen which react with potassium hydroxide in the following manner: if the acid be represented as HpA it reacts with p equivalents of potassium hydroxide KOH to form KpA and water only?" Owing to its brevity, many beginners would be satisfied with the sentence on page 2 that "Salts are compounds derived from acids," although the author discusses the idea of replaceable hydrogen in the next sentence.

However, this small digest of facts will undoubtedly serve a useful purpose. The chapters are composed of brief, numbered paragraphs with the topic to be discussed set in bold type. The book presents a pleasing appearance.

WM. LLOYD EVANS.

Manual of Quantitative Chemical Analysis. By J. O. FRANK AND E. A. CLEMANS. Oshkosh, Wis. Castle-Pierce Printing Co. 1914. 12 + 123 pp. Price, \$1.25.

This is a small, pocket-size book which, according to the preface, lays claim to being a laboratory manual only. This idea is consistently carried out, for the general descriptive matter is given in the merest outline. The deficiency is made up in a way by references to larger text-books; an excellent plan, if only there is a sufficiently large number of reference books at hand or a sufficiently small number of students to use them.

There are forty-nine laboratory exercises divided among gravimetric, electrolytic, volumetric and gas analysis. Twenty-two of these exercises call for the determination of some constituent of a pure salt, for example

copper in copper sulfate. The remainder of the list consists of methods for the preparation and standardization of volumetric solutions and for the analysis of commercial samples.

A systematic plan is used in presenting these laboratory exercises. There is first a short list of references to large text-books followed by a paragraph marked "Theory," in which a brief, general outline of the method is given. Next comes the "Method," the directions for carrying out the experimental work of the analysis in question. Finally there is a short list of questions followed by the chemical equations involved. This scheme of presentation and the concise directions for the laboratory work are the important features of the book.

The number and choice of the laboratory exercises to be used in the first year of quantitative work are a matter of opinion. Some prefer a large number of exercises containing many examples of pure salts, while others prefer a smaller number made up mostly of commercial samples, each exercise to be studied in detail. Those teachers who, like the authors, prefer a long list of determinations will do well to look into this little manual.

The book is, however, marred by the obvious failure to go through the proof sheets and eliminate such blunders as "dessicator" and such laboratory colloquialisms as "Using the result of your titration calculate the strength of your acid." The same carelessness is shown in not always looking up modern practice. On page 64 it is directed, in the emptying of a pipet, "to blow once or twice." To blow once is bad enough, but to leave the poor student the choice of blowing once or twice—! The above are typical of a large number of cases that detract from an otherwise good laboratory manual. Perhaps, though, the reviewer feels too strongly that there should be a direct relation between the accuracy of scientific work and the accuracy of writing about it. C. W. FOULK.

Principles of Quantitative Analysis. An Introductory Course. By WALTER C. BLASDALE, Associate Professor of Chemistry in the University of California. D. Van Nostrand Company, New York. 1914. x + 394 pp.; 70 ills. Price, \$2.50 net.

In this work the author presents the fundamental principles of quantitative analysis, and outlines a method by which a working knowledge of the subject can be attained. This is done by a scheme of classification, which is based upon the different types of chemical and physical equilibria.

The subject matter is arranged in ten sections as follows: 1. General features of gravimetric processes, 77 pp. 2. Gravimetric gas-evolution processes, 33 pp. 3. Gravimetric precipitation processes, 84 pp. 4. Gravimetric solution and extraction processes, 21 pp. 5. Partition processes, 14 pp. 6. General features of volumetric processes, 22 pp. 7.

Volumetric processes involving precipitation, 21 pp. 8. Volumetric processes involving neutralization, 33 pp. 9. Volumetric processes involving oxidation, 44 pp. 10. Physico-Chemical processes, 31 pp.

In the first section the author discusses many things of a general nature which pertain to quantitative chemistry, such as weighing, solutions, electrolytes, calculation of results, etc.

In presenting the quantitative procedures which follow the introduction, the theory of each process is discussed from the point of view of modern theoretical chemistry. Then some typical illustrations are given in considerable detail, with questions and problems appended which may be assigned to the students for solution.

The book contains the most important facts and theories of quantitative chemistry very well arranged and clearly stated. The most notable feature of the work is the special attention given to theory, much more of it having been introduced than is generally found in text books on quantitative analysis. The author states, "It is only through a definite knowledge of the theory of each step of the process that the analyst can work intelligently and effectively; the mechanical performance of such operations without understanding the reason for each step is not worthy of being dignified by the term 'quantitative analysis.'" This attitude toward the work is certainly the proper one, but it is feared that the author in his endeavor to emphasize this feature of the work has included some theoretical matter too advanced for the beginner in quantitative analysis. The subject matter, however, is so systematically arranged, with the greater part of the theory placed at the beginning of each section forming a separate part, that more or less of it can be considered, as desired.

The minerals, ores, alloys and products selected for analyses are substances which the chemist is likely to meet in ordinary practice and vary sufficiently to give the student a variety of principles and methods of procedure. The methods selected are standard ones and are clearly and accurately described with sufficient detail.

The questions and problems following the procedures have been well selected and emphasize the general principles made use of in the work.

References to original papers relating to many of the processes described are given.

The student who masters the contents of this book will certainly obtain a thorough foundation in quantitative analysis. C. F. SIDENER.

Monographs on Inorganic and Physical Chemistry. Intermetallic Compounds. By CECIL H. DESCH, D.Sc., Ph.D., F.I.C. pp. vi + 116. Longmans, Green & Co., London, New York. Price, 90 cents.

Dr. Desch has accomplished a very useful piece of work in placing before the public in so concise and complete a form the data collected

in this field. To anyone who has not followed the recent literature on alloys, this small volume will be a surprise as to the extent of the work accomplished. The collection of data of this kind and the digestion of the literature is extremely helpful to those not making a specialty of the subject. The book is limited in its scope to the properties of and identification of compounds between metals, and assumes that the reader can interpret an equilibrium diagram.

The subjects discussed are: Thermal Analysis; The Principal Method for Identifying Intermetallic Compounds; Microscopic Structure; The Isolation of Intermetallic Compounds; Physical Properties; The Existence of Intermediate Compounds in the Liquid State; The Relations of Intermetallic Compounds to Carbides, Silicides, etc., and the Chemical Nature of such Compounds; Ternary Compounds.

The book is clearly written, well illustrated with diagrams, and a useful list of references is given.

HENRY FAY.

Outlines of Organic Chemistry. By F. J. MOORE, Professor of Organic Chemistry in the Massachusetts Institute of Technology. Second edition, rewritten. New York: John Wiley & Sons. 1914. xi + 325 pp. Price, \$1.50.

The present book, as suggested by the author, arose out of a course of lectures delivered almost exclusively to candidates for the bachelor's degree in Physics, Biology and Sanitary Engineering. An attempt has been made to present a "selection of topics which is somewhat different from that given to those who are fitting themselves to become organic chemists." The compounds discussed are selected because of their so-called practical importance or because of their convenient illustrative value in presenting fundamental principles.

Many topics of interest in organic chemistry, such as the synthesis of aceto-acetic ester, the Grignard reaction, etc., are omitted as not being of sufficiently vital interest to the classes of students concerned. In the case of simpler compounds, constitutional proof is presented in considerable detail. In other cases the author has avoided elaborate discussion and in some, the formulae alone are given.

Following the introduction there is given in Chapters 2-6, an elementary consideration of the saturated hydrocarbons, alcohols, acids, aldehydes, ketones, amines and unsaturated hydrocarbons. More complex organic compounds are presented in Chapters 7-11, followed in Chapter 12 by a discussion of the chemistry of certain vital processes. In Chapters 13-18 aromatic hydrocarbons and their simple derivatives are presented and in the concluding chapter, a brief discussion of the theory of structure.

In considering his treatment of the subject one cannot but feel that the author might, with advantage, have drawn a little more fully upon illustrative material, particularly from the field of applied chemistry. This would have much enhanced the interest of the work without unduly lengthening

the book. Of advantage, furthermore, would have been the addition of lists of suggestive questions and problems at the close of the several chapters.

Dr. Moore has, however, produced a book which is well written and clear in the exposition of the subject matter. As a brief introduction to organic chemistry, it merits the attention not only of the class for whom it was designed, but also of those who intend to devote their attention more fully to pure chemistry.

H. C. BIDDLE.

A Study of Foods. By RUTH A. WARDALL AND EDNA N. WHITE. Boston, Mass.: Ginn & Company. 174 pp. Price, 70 cents.

This is an elementary treatment of foods and is primarily suited for teachers of food courses in secondary and extension schools. It should also be found useful in the home. The treatment of the subject matter is simple and non-technical; in fact no chemical formulation is found. There are 22 chapters with a brief description of the common food constituents given in the first chapter. The next 18 chapters are devoted to the natural food materials themselves and their uses in the dietary. The 3 additional chapters relate to food requirements, selection of foods and serving of meals. In many instances one wishes that the treatment might have been more extensive, for the authors write with clearness and accuracy of statement. Rarely is there to be found any of the fads and notions prevalent about foods.

On page 5 occurs the statement "heavy eating of meat may easily furnish more protein than is desirable and it is believed that meat protein may cause more harm than other proteins," for which we might ask for definite proof.

This work is more than a book of recipes, yet combines briefly the usefulness of the recipe book with descriptions of the properties and general composition of the foods themselves.

Appended to each chapter is a helpful list of references. The illustrations are good and the printing and book make-up all that could be desired.

E. B. HART.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY
OF ILLINOIS.]

**A STUDY OF THE SYSTEM: WATER, POTASSIUM IODIDE AND
IODINE AT ZERO DEGREES.**

BY GRINNELL JONES AND MINER LOUIS HARTMANN.

Received November 30, 1914.

This investigation was undertaken as a necessary preliminary step in the study of the temperature coefficient of the free energy of formation of silver iodide from its elements. The method of procedure in determining this free energy was to measure the electromotive force of cells in which silver iodide is reversibly formed from silver and iodine at 0° and 25° . One-half of these cells consisted of a silver electrode surrounded with solid silver iodide immersed in a dilute potassium iodide solution; the other half consisted of a platinum electrode surrounded by solid iodine immersed in a saturated solution of iodine in dilute potassium iodide solution.

In order to apply a correction for the potential at the boundary of the two solutions and a correction for osmotic work involved in the operation of the cell, it is necessary to know the concentration and mobility of the potassium, iodide and tri-iodide ions present in each half of their cell at two different temperatures.

The necessary information in regard to the ionic mobilities and concentrations at 25° is furnished by the investigation of Bray and MacKay.¹

¹ W. C. Bray and G. M. J. MacKay, *THIS JOURNAL*, **32**, 914 (1910); W. C. Bray, *Ibid.*, **32**, 932 (1910).

No other temperature is known to us.¹ It was, therefore, decided to make dilute potassium iodide solutions saturated with iodine at 0°. This study necessarily follows closely the methods used by Bray and MacKay, both in experimental procedure and in the interpretation of the results. It is a pleasure to acknowledge our indebtedness to these authors for many valuable suggestions. We introduced a number of variations in the experimental methods, some of which were required because we were making our measurements at 0°, but with one exception these variations were probably without significant effect on the results. This exception is the determination of the change in viscosity caused by the solution of potassium iodide and of potassium iodide plus iodine in water. As will be shown more in detail in the following pages, a 0.1 *N* solution of potassium iodide has a viscosity only 0.982 of the viscosity of pure water at the same temperature. Therefore, the degree of dissociation of potassium iodide would be overestimated by about 1.8% by the usual method of calculation. After this solution is saturated with iodine at 0°, its viscosity is raised to 0.995 of that of water. Therefore, the change in conductivity when iodine is dissolved in potassium iodide solutions is not due wholly to the replacement of part of the iodide ion by the tri-iodide ion, but partly to a slower motion of all of the ions present. Bray and MacKay neglected this influence, but, fortunately, the error caused thereby at 25°, although greater than the other errors in the work of Bray and MacKay is much less than the errors which would have been caused at 0° by the neglect of this correction. Of course the influence of the change in viscosity is less with the weaker solutions.

Purification of Materials.

Water.—All of the water used in this investigation, either in the purification of chemicals or in making the solutions, was conductivity water obtained from the special still² in this laboratory. The distillation was made from alkaline permanganate solution, and only the middle portion was collected for use. It was collected hot in previously steamed bottles of "non-sol" glass. The specific conductance of this water prepared at different times varied from 0.24×10^{-6} to 0.7×10^{-6} at 0°.

Iodine.—Iodine was prepared by dissolving "C. P." resublimed iodine in a very concentrated potassium iodide solution, diluting and distilling off the iodine. It was then washed with water on a Büchner funnel to remove any salts which might have spattered over during distillation,

¹ H. M. Dawson, *J. Chem. Soc.*, **79**, 239 (1901), has studied the equilibrium $KI + I_2 \rightleftharpoons KI_3$ at 13.5°, but his purpose did not require the measurement of the electrical conductivity of his solutions.

² Our still was patterned after the one described by Noyes and Coolidge, *Proc. Am. Acad.*, **39**, 190 (1910).

and then reduced to hydriodic acid by adding yellow phosphorus. The reaction went very smoothly; after standing on the steam bath for a short time the solution was completely decolorized. The hydriodic acid was separated from acids containing phosphorus by distillation. The solution being more dilute than the constant boiling mixture, water came off first, and this fraction must have contained all the hydrocyanic acid, if any were formed during the process.¹ Acid boiling from 123° to 135° was collected.

The iodine was liberated from a portion of this acid by action of halogen-free potassium permanganate and sulfuric acid.² The precipitated iodine was thoroughly washed with water in a Büchner funnel and dried in a desiccator over sulfuric acid for nearly a year before use. A short time before use this iodine was resublimed in a current of dry air, the condenser consisting of a hard glass tube which fitted into the subliming apparatus by a ground glass joint.

Potassium iodide.—Another portion of the hydriodic acid, prepared as described above, was redistilled, reserving only the portion which distilled over between 125° and 127° for use in making potassium iodide. Kahlbaum's potassium bicarbonate, which contained some normal carbonate but no halogens, and which showed only a trace of sodium by the flame test, was recrystallized by dissolving in hot water, cooling and passing in pure carbon dioxide. This gave a mixture of carbonate and bicarbonate, which was dried centrifugally³ in platinum Gooch crucibles. It gave no flame test for sodium after this treatment. The hydriodic acid was added in slight excess and the solution concentrated by evaporation. The potassium iodide was then crystallized by cooling and the salt dried centrifugally. The salt had a slight yellow color due to free iodine. It was heated on an electric stove at 60° for twenty-four hours to drive off water, hydriodic acid and iodine. The salt thus prepared was perfectly white and when dissolved in water gave a solution which was neutral and contained no free iodine and no iodate. It was found to be unsafe to heat the salt above 60° because iodine is liberated and it becomes alkaline.

Experimental Methods.

The Preparation of the Standard Potassium Iodide Solutions.

The potassium iodide was dried to constant weight at 60° by reheating for several hours in the weighing bottle on an electric stove. It was then

¹ Commercial iodine sometimes contains traces of iodine cyanide which may be eliminated as described above. See G. P. Baxter, *Proc. Am. Acad. Arts and Science*, 40, 421 (1904).

² A little manganese peroxide was precipitated with the iodine owing to failure to secure the best proportions of the reagents. It was, however, completely separated later by subliming the iodine.

³ G. P. Baxter, *THIS JOURNAL*, 30, 287 (1908).

weighed and dissolved in a "non-sol" glass bottle in conductivity water to make a solution approximately 0.1 *N* and the exact weight of the solution was determined.¹

The mols of potassium iodide per thousand grams of solution is called the weight normality of the solution. The density of this solution at 0° was carefully determined in order that the mols per liter or volume normality could be calculated. The density determinations were made in a pycnometer of the familiar Ostwald-Sprengel type, which was modified by the addition of a small bulb in the larger capillary tube beyond the graduation mark, of sufficient capacity to prevent loss of liquid owing to expansion when the solution was warmed to room temperatures for weighing. It was provided with a ground glass cap over the capillary tip to prevent evaporation. It had a volume slightly greater than 26 cc. and its weight when filled to the mark was concordant on successive trials to within 0.5 mg., or about 2 parts in one hundred thousand. A similar pycnometer was used as a counterpoise when weighing.

All solutions weaker than 0.1 *N* were prepared by dilution of a stronger solution by weight rather than by volume. Conductivity water was added to a known weight of a standard solution in a "non sol" bottle and the weight of the more dilute solution determined. The volume normality of the diluted solution at 0° was calculated with the help of the density. This procedure is more accurate than dilution by means of pipets, since the results are not influenced by uncertainties in drainage or temperature. These advantages are especially marked if it is necessary to know the concentration of solutions at temperatures far removed from room temperatures.

Conductance Measurements.

The conductance measurements were made by means of a slide-wire bridge of the roller type made by Leeds & Northrup. The bridge wire was manganin about two meters long with scale divisions of approximately three millimeters. The bridge wire was calibrated against the resistances of two Leeds & Northrup decade boxes, which had been standardized by the Bureau of Standards. The resistances used were made of manganin wire wound according to the Chaperon² principle to reduce self-induction and static capacity. These resistances were checked against standard resistance boxes and were found to be free from significant errors. A small condenser was used, when necessary, to balance the capacities of the resistance box and the conductivity cell, as recommended by Kohlrausch and Holborn.

A commutating device on the bridge allowed the ends of the wire to be reversed or commutated, and this was done in every case, although

¹ All weights have been corrected to vacuum.

² Chaperon, *Compt. rend.*, 108, 799 (1889); Kohlrausch and Holborn, p. 58.

no variation in resistance was found by reversing the position of the resistance box and the conductance cell. Readings on the bridge were reproducible to one part in five thousand. The conductance cells were of the pipet type.¹ The cell constants were determined exactly according to the directions of Kohlrausch and Holborn, "Leitvermögen der Elektrolyte." The constant of No. 1 was found by E. K. Strachan to be 4.077 at 0°, using both 1 *N* and 0.1 *N* potassium chloride. We determined the constant of No. 2 using 0.1 *N* potassium chloride and found it to be 0.6222, which agrees exactly with the result of Washburn and MacInnes on the same cell obtained a year before. The constant of cell No. 3 was determined to be 0.06198 by comparison with No. 2 by using the same dilute solution in both cells. This result agreed exactly with that obtained by C. G. Derick, using 0.01 *N* potassium chloride. The conductance of the water used was determined by means of a cell with platinum-iridium electrodes about 3 cm. in diameter and 1 mm. apart. The surfaces of these electrodes were sand-blasted, but not covered with platinum black. The constant of this cell was 0.0294.

The conductance cells were kept during measurement in large Dewar tubes filled with distilled water and finely cracked ice made from distilled water.

An approximate setting having been made on the bridge, sufficient time was allowed to insure that the cell was at 0°, and then the final adjustment was made. This precaution was necessary because the solutions, especially the concentrated ones, became heated by the current from the induction coil, thereby decreasing the resistance. In all cases the ends of the bridge were commutated and readings made with the resistance in the box both higher and lower than the resistance of the solution in the other arm of the bridge. These values agreed within 0.1%.

The specific conductance of the water used in making the solutions was always measured and subtracted from the observed conductance of the solutions. This was never larger than 0.7×10^{-6} at 0°.

Saturation of the Potassium Iodide Solutions with Iodine.

The saturation of the potassium iodide solution with iodine was accomplished by shaking the solution with an excess of iodine in 250 cc. "non sol" glass-stoppered bottles in a shaking machine working in a bath of finely cracked ice and distilled water. The shaking was accomplished by means of a simple reciprocating motion from a crank on a fly wheel, and driven at high speed by a motor. The piston rod was supported

¹ See E. W. Washburn and D. A. MacInnes, *THIS JOURNAL*, 33, 1688-9 (1911) for a diagram and description of the type of cell used. These authors point out that this type of cell has important advantages over the usual form. Our cell No. 2 was the same as Washburn and MacInnes' cell No. 2. Our Nos. 1 and 3 were similar to theirs, but not the identical cells.

at an angle in order to secure the greatest efficiency in stirring in the bottle. The machine made about 200 strokes per minute. After the bottle was filled almost full of the solution under investigation, and an excess of solid iodine had been added, the stopper was inserted and a rubber "cap" was then slipped over the stopper and neck of the bottle and wired on to prevent the water of the ice bath from reaching the ground glass joint. The bottle was shaken in the ice bath for one and a half hours or more. Experiments were made which showed that this amount of shaking gave complete saturation.

After saturating with iodine, the electrical conductivity, density and free iodine dissolved were determined. The bottle was first allowed to stand for a short time to allow the iodine to settle and then the conductance cell was filled directly from the bottle without filtering, since the presence of particles of solid iodine could do no harm. A portion for the density determination was forced by air pressure through a tube containing a small bulb filled with tightly packed asbestos, which served as a filter, into a beaker cooled with ice and from this at once transferred to the pycnometer.¹ Several portions of the solution for analysis were forced in the same manner into weighed glass-stoppered flasks. The filtering bulb was below the liquid in the shaking bottle, and so it was always at 0°, thus preventing any warming of the solution while in contact with solid iodine. The flasks containing these samples were allowed to warm up to room temperature, and were then weighed. They were then cooled again with ice to condense the iodine vapors before the flasks were opened for titration, in order to avoid loss of iodine. In the later experiments several grams of solid potassium iodide were added to the flask and weighed with it before the sample was forced into the flask. This reduced the vapor pressure of iodine and thus served to prevent loss.

The free iodine was titrated by means of standard solutions of sodium arsenite containing a large amount of monosodium and disodium phosphates in the proportions recommended by Washburn,² who has clearly demonstrated that this is a very accurate titration when carried out under the proper conditions. Two solutions about 0.15 *N* and 0.007 *N*, respectively, were used. These titrations were carried out entirely by means of weight burets for the sake of accuracy, the final approach to the end point being accomplished with the dilute solution. In rare cases the end point was passed accidentally and in these cases a dilute iodine solution, approximately 0.006 *N*, was used. This solution was standardized against the dilute arsenite solution. These arsenite solutions were standardized against known weights of pure dry iodine, the weighing

¹ The first 5 or 10 cc. which came through were always rejected.

² E. W. Washburn, *THIS JOURNAL*, 30, 31 (1908); Washburn and Bates, *Ibid.*, 34, 1355 (1912).

bottle being opened under the arsenite solution to prevent loss of iodine. These standardizations were concordant within 0.02%, which was ample for the present purpose.

We found that a very satisfactory method of determining when the iodine was all reduced was to titrate until the very faintest yellow color remained. Then about 5 cc. of pure benzene were added and the solution shaken violently. The small trace of iodine dissolved in the benzene gave a pink color, which could be easily seen. Dilute arsenite solution was then added drop by drop until the pink color in the benzene layer had disappeared after shaking.

Viscosity Measurements.

The viscosity measurements were very kindly made for us by G. Y. Williams.¹ The viscosities of potassium iodide solutions approximately 0.1 *N* and 0.05 *N* were measured at 0° (see Table III, Column 5, for the results) and at 25° (Table IV, Column 5) and then these solutions were saturated with iodine at 0° and the viscosity determined again at 0° (Table III, Column 9) and at 25°. Since these solutions were not quite saturated at 25°, a slight correction has been made on the assumption that the small additional amount of iodine had the same proportional effect on the viscosity. The results are given in Table IV, Column 9. It is believed that these viscosity data are accurate within 0.1%.

TABLE I.—THE EXPERIMENTAL DATA.

| First Series. | | | | | | | | |
|-------------------|-----------|----------------|----------------|--------------------------------------|----------------|-------------------------|-----------------------------|--------------------|
| Potassium iodide. | | | | Saturated with iodine. | | | | |
| No. | Wt. norm. | Density 0°/4°. | Vol. norm. 0°. | Specific conductance $\times 10^6$. | Density 0°/4°. | Gram iodine per g. sol. | Spec. cond. $\times 10^6$. | Σ K vol. norm. 0°. |
| 1 | 0.09861 | 1.01231 | 0.09982 | 7340.7 | 1.02187 | 0.01199 | 6412.9 | 0.09956 |
| 2 | 0.04966 | 1.00610 | 0.04996 | 3765.2 | 1.01089 | 0.006083 | 3308.4 | 0.04989 |
| 3 | 0.01992 | 1.00236 | 0.01997 | 1549.6 | 1.00429 | 0.002535 | 1365.8 | 0.019957 |
| 4 | 0.00998 | (1.0011) | 0.009993 | 789.2 | (1.0020) | 0.0013546 | 694.0 | 0.009990 |
| | | | | | | 0.0013518 | 692.0 | |
| 5 | 0.004991 | (1.0005) | 0.004993 | 400.1 | (1.0011) | 0.0007574 | 352.8 | 0.004992 |
| | | | | | | 0.0007580 | 352.9 | |
| 6 | 0.002000 | (1.0001) | 0.002000 | 162.31 | (1.0004) | 0.0004074 | 142.9 | 0.002000 |
| | | | | | | 0.0004238* | 142.8 | |
| | | | | | | 0.0004099 | | |
| 7 | 0.000992 | (1.0000) | 0.000992 | 81.19 | (1.0002) | 0.0002823 | 71.9 | 0.000992 |
| | | | | | | 0.0002802* | 72.0 | |

* Not included in summary Table III. Numbers in parentheses are interpolated values.

¹ See Washburn and Williams, *THIS JOURNAL*, 35, 737 (1913) for a description of the method. These measurements were made in the early stages of their investigation described in this paper and before all of the experimental details had been perfected.

TABLE II.—EXPERIMENTAL DATA

| Potassium iodide. | | | | Second Series. | | | | Saturated with iodine. | | |
|-------------------|-----------|----------------|------------|--------------------------------------|----------------|-----------------------|-----------------------------|------------------------|--|--|
| No. | Wt. norm. | Density 0°/4°. | Vol. norm. | Specific conductance $\times 10^4$. | Density 0°/4°. | G. iodine per g. sol. | Spec. cond. $\times 10^4$. | ΣK vol. norm. | | |
| 8 | 0.09871 | (1.0123) | 0.09993 | 7341.1 | (1.0219) | 0.01199 | 6403.6 | 0.09966 | | |
| 9 | 0.04937 | (1.0061) | 0.05000 | 3753.7 | (1.0109) | 0.006088 | 3297.6 | 0.04992 | | |
| | | | | | | 0.006100* | 3296.5 | | | |
| 10 | 0.01981 | (1.0024) | 0.01999 | 1538.3 | (1.0044) | 0.002533 | 1353.5 | 0.01987 | | |
| | | | | | | | 1353.1 | | | |
| 11 | | | | | | | 601.2 | 0.01000 | | |
| | | | | | | | 697.2 | | | |
| 12 | 0.004999 | (1.0005) | 0.005001 | 399.90 | (1.0010) | 0.0007586 | 352.6 | 0.005000 | | |
| | | | | | | | 352.6 | | | |
| 13 | 0.002000 | (1.0001) | 0.002000 | 162.16 | (1.0004) | 0.0004021 | 143.31 | 0.002000 | | |
| | | | | | | 0.0004009 | 143.5 | | | |
| 14 | 0.000999 | (0.9999) | 0.000999 | 81.72 | (1.0002) | 0.0002869 | 72.3 | 0.000999 | | |
| | | | | | | 0.0002823 | 71.9 | | | |
| | | | | | | 0.0002825 | 72.0 | | | |

* Not included in summary Table III.

The Experimental Data.

The experimental data for the solubility, density and conductance are shown in Tables I and II. The figures for the conductance are the averages obtained by commutating the bridge-wire and changing the resistance used. The figures for the solubility of iodine are the averages obtained by titrating two or three portions of the same solution. When more than one set of data is given for the solutions, saturated with iodine, they represent separate saturations with iodine of the corresponding potassium iodide solutions. Except in a very few cases, the conductance data are concordant within 0.1%. The solubility data do not agree so well, discrepancies of 0.2% being common. In a few cases discrepancies up to 1%, and in one case up to 4%, were encountered, but a repetition of the experiment and a plot of the results at different concentrations enables us to reject the erroneous results. These occasional erratic results were probably due to small particles of solid iodine passing the filters. Bray and MacKay¹ also found it impossible to secure as great conductance in the solubility data as in the conductance data.

The last column gives the volume normality of the solutions saturated with iodine corrected for the change in volume, which occurs when iodine is dissolved.

The solubility of iodine in mols I_2 per liter in potassium iodide solutions at 0° is expressed within the limit of error of our experiments up to and including 0.05 *N* by the linear equation, $(I_2) = 0.000638 + 0.472 c$, *c* being the concentration of the potassium iodide solution. A 0.1 *N*

¹ Bray and MacKay, *This Journal*, 32, 919 (1910).

solution dissolves about 1% more iodine than the result given by this equation.

The density determinations were carried out with the three strongest solutions only, because the density was found to be a linear function of the concentration with an accuracy much surpassing our needs. For potassium iodide solutions

$$d^{0^{\circ}}_{4^{\circ}} = 0.99987 + 0.1246 c.$$

For the same solutions saturated with iodine,

$$d^{0^{\circ}}_{4^{\circ}} = 0.99987 + 0.2205 c.$$

The Equivalent Conductance of Potassium Iodide.

In order to simplify the interpretation and use of the experimental data, the results of the two series have been rounded off to even concentrations by volume, as shown in Table III. Experimental results which were known to be in error, and in a few cases data which for some unknown reason were obviously discordant with the other data, have been rejected in deriving this summary table. Column 3 gives the equivalent conductance of potassium iodide solutions at 0°. Similar measurements have been made by Sloan,¹ Kahlenberg,² and Harry C. Jones.³ These results have all been plotted (log C against Λ and by the Noyes method $1/\Lambda$ against $(CA)^{n-1}$) for comparison. Sloan's measurements extend from 0.04235 *N* to 5.1 *N*. In the small range where our measurements overlap with Sloan's, his values for Λ are about 0.2 higher than ours, and our results may be regarded as an extension of Sloan's curve into more dilute solutions. The curve (log C against Λ) representing Kahlenberg's results is very irregular, having two well-marked points of inflection in marked contrast to the curve representing our results, which has none.⁴ Three of Kahlenberg's points ($C = 1/32, 1/64, 1/128$) fall near our curve, but the others are about 1 to 1.15 units on the conductance lower than ours and Sloan's. The curve representing Harry C. Jones' results is lower than ours by 4 or 5 units of the equivalent conductance or about 6%. The measurements of Harry C. Jones on potassium iodide at 25° are lower than those of Bray and MacKay at 25° by about the same per cent.

The equivalent conductance of potassium iodide at infinite dilution has been found to be 83.5 by the plotting of $1/\Lambda$ against the corresponding value of $(CA)^{n-1}$, as proposed by A. A. Noyes.⁵ The value of n was found by trial plots using several values from $n = 1.3$ to $n = 1.6$, and choosing $n = 1.45$ as the exponent which gave the best straight line through

¹ W. H. Sloan, *THIS JOURNAL*, **32**, 946 (1910).

² L. Kahlenberg, *J. Phys. Chem.*, **5**, 348 (1901).

³ H. C. Jones, *Carnegie Inst. of Washington Pub.*, **170**, 21 (1912).

⁴ See Noyes and Falk, *THIS JOURNAL*, **34**, 473 (1912), footnote 13.

⁵ A. A. Noyes, *THIS JOURNAL*, **31**, 745 and 1010 (1909); Carnegie Publication No. 63.

TABLE III.
This table applies at 0°.

| 1. Vol. norm. KI. | 2. Density 0°/4°. | 3 Akt. | 4. 100 γ KI not corrected. | 5. η/η_0 KI. | 6. $\Delta\eta/\eta_0$ KI. | 7. 100 γ KI corr. for viscosity. | 8. Λ KI + KI ₂ . | 9. η/η_0 KI + KI ₂ . | 10. $\Lambda\eta/\eta_0$ KI + KI ₂ . | 11. $\Delta\Lambda$. |
|-------------------------|-------------------------|-----------|--|----------------------------|----------------------------------|---|---|---|---|--------------------------|
| 0.1 | 1.0124 | 73.5 | 88.0 | 0.982 | 72.2 | 86.4 | 64.35 | 0.995 | 64.05 | 8.15 |
| 0.05 | 1.0061 | 75.2 | 90.1 | 0.991 | 74.5 | 89.25 | 66.2 | 0.9975 | 66.05 | 8.45 |
| 0.02 | 1.0023 | 77.5 | 92.8 | 0.996 | 77.2 | 92.45 | 68.25 | 0.999 | 68.2 | 9.05 |
| 0.01 | 1.0011 | 78.85 | 94.5 | 0.998 | 78.7 | 94.3 | 69.4 | 0.9995 | 69.4 | 9.3 |
| 0.005 | 1.0005 | 80.05 | 95.8 | 0.999 | 80.0 | 95.8 | 70.6 | 1.000 | 70.6 | 9.4 |
| 0.002 | 1.0001 | 81.1 | 97.2 | 0.9996 | 81.05 | 97.1 | 71.55 | 1.000 | 71.5 | 9.55 |
| 0.001 | 1.0000 | 81.8 | 98.0 | 0.9998 | 81.8 | 98.0 | 72.2 | 1.000 | 72.2 | 9.6 |
| 0.000 | .. | 83.5 | 100.0 | .. | 83.5 | ... | .. | .. | .. | 9.8 |

| 12. ΣK. | 13. ΣKI ₂ + I ₂ . | 14. ΣI ₂ . | 15. ΣI. | 16. $r = \Sigma I_2 / \Sigma K.$ | 17. $\Delta\Lambda/r$. | 18. Λ KI ₂ corr. | 19. γ KI ₂ corr. | 20. I^- . | 21. I_2^- . | 22. I^-/I_2^- . | 23. $(I^-)(I_2)/I_2^-$. |
|------------|--|--------------------------|------------|-------------------------------------|----------------------------|---|--|----------------|------------------|----------------------|-----------------------------|
| 0.1 | 0.09973 | 0.04833 | 0.04769 | 0.05204 | 0.478 | 55.15 | 87.7 | 0.04498 | 0.04181 | 1.076 | 686 × 10 ⁻⁸ |
| 0.05 | 0.04993 | 0.02426 | 0.02362 | 0.02631 | 0.473 | 56.6 | 90.0 | 0.02348 | 0.02125 | 1.105 | 705 |
| 0.02 | 0.01999 | 0.01006 | 0.00942 | 0.01057 | 0.471 | 58.1 | 92.4 | 0.00977 | 0.00870 | 1.123 | 716 |
| 0.01 | 0.009996 | 0.005354 | 0.004716 | 0.005280 | 0.472 | 59.0 | 93.8 | 0.004976 | 0.004423 | 1.125 | 718 |
| 0.005 | 0.004999 | 0.002993 | 0.002355 | 0.002644 | 0.471 | 60.1 | 95.4 | 0.002533 | 0.002246 | 1.128 | 720 |
| 0.002 | 0.002000 | 0.001582 | 0.000944 | 0.001056 | 0.472 | 60.85 | 96.7 | 0.001025 | 0.000913 | 1.123 | 717 |
| 0.001 | 0.001000 | 0.001113 | 0.000475 | 0.000525 | 0.475 | 61.6 | 97.8 | 0.000514 | 0.000464 | 1.108 | 707 |
| 0.000 | 0.000000 | 0.000638 | | | 0.472 | 62.9 | ... | | | ... | .. |

TABLE IV.
This table applies at 25°. Data from Bray and MacKay, THIS JOURNAL, 32, 914, corrected for viscosity.

| 1. Vol. norm. KI. | 2. Density. | 3. $\Delta\kappa_i$. | 4. 100 γ KI not corrected. | 5. η/η_0 KI. | 6. $\Delta\eta/\eta_0$ KI. | 7. 100 γ KI corr. for viscosity. | 8. Λ KI + KI ₂ . | 9. η/η_0 KI + KI ₂ . | 10. $\Delta\eta/\eta_0$ KI + KI ₂ . | 11. $\Delta\Lambda$. | |
|---------------------------|---------------------------------|--------------------------|--|---|----------------------------------|---|---|---|--|--------------------------|--|
| 0.1 | | 130.8 | 86.5 | 0.994 | 130.0 | 85.9 | 115.25 | 1.003 | 115.6 | 14.4 | |
| 0.05 | | 137.7 | 89.1 | 0.997 | 134.3 | 88.8 | 118.8 | 1.0015 | 119.0 | 15.3 | |
| 0.02 | | 139.4 | 92.1 | 0.999 | 139.3 | 92.05 | 123.45 | 1.0005 | 123.5 | 15.8 | |
| 0.01 | | 142.3 | 94.1 | 0.9995 | 142.25 | 94.0 | 126.0 | 1.000 | 126.0 | 16.25 | |
| 0.005 | | 144.5 | 95.5 | 1.000 | 144.5 | 95.5 | 128.2 | 1.000 | 128.2 | 16.3 | |
| 0.002 | | 146.7 | 97.0 | 1.000 | 146.7 | 97.0 | 130.4 | 1.000 | 130.4 | 16.3 | |
| 0.001 | | 147.9 | 97.8 | 1.000 | 147.9 | 97.8 | 131.7 | 1.000 | 131.7 | 16.2 | |
| 0.000 | | 151.3 | 100.0 | .. | 151.3 | ... | .. | .. | .. | ... | |
| 12. $\Sigma\kappa_i$. | 13. $\Sigma\kappa_1 + I_2$. | 14. ΣI_2 . | 15. ΣI_1 . | 16. $r = \Sigma I_2 / \Sigma \kappa_i$. | 17. $\Delta\Lambda/r$. | 18. Λ KI ₂ corr. | 19. γ KI ₂ corr. | 20. I^- . | 21. I_2^- . | 22. I^-/I_2^- . | 23. $(I^-)(I_2)/I_2^- \times 10^{-6}$. |
| 0.1 | 0.09969 | 0.03135 | 0.05003 | 0.04966 | 0.502 | 28.7 | 101.3 | 87.5 | 0.04267 | 0.04377 | 1287 |
| 0.05 | 0.04992 | 0.02577 | 0.02445 | 0.02547 | 0.497 | 30.8 | 103.5 | 89.4 | 0.02261 | 0.02185 | 1366 |
| 0.02 | 0.01999 | 0.01113 | 0.00981 | 0.01018 | 0.491 | 32.2 | 107.1 | 92.5 | 0.00937 | 0.00907 | 1363 |
| 0.01 | 0.01000 | 0.006185 | 0.004865 | 0.005135 | 0.486 | 33.45 | 108.8 | 94.0 | 0.004827 | 0.004571 | 1394 |
| 0.005 | 0.00500 | 0.003728 | 0.002408 | 0.002592 | 0.482 | 33.8 | 110.7 | 95.6 | 0.002475 | 0.002302 | 1420 |
| 0.002 | 0.00200 | 0.002266 | 0.000946 | 0.001054 | 0.473 | 34.5 | 112.2 | 96.9 | 0.001022 | 0.000917 | 1472 |
| 0.001 | 0.00100 | 0.001788 | 0.000468 | 0.000532 | 0.468 | 34.6 | 113.3 | 97.8 | 0.000520 | 0.000458 | 1499 |
| 0.000 | | 0.00132 | | ... | ... | 115.8 | 100.0 | | | .. | .. |

the points. This was also shown to be the best line by calculating the deviations by the method of least squares. The first series gave $\Lambda_0 = 83.47$ and the second series $\Lambda_0 = 83.49$. The rounded-off value 83.5 is accepted.

This method is purely empirical and every one who has used it has recognized that the results obtained with it are open to some doubt. Recently Bates¹ has argued that the values of Λ_0 obtained by this method are too high by about 0.5%. Still more recently Kraus and Bray² have proposed a general equation for the relationship between ionization and concentration of solutions, which they consider applicable to all solutions, both dilute and concentrated, aqueous and non-aqueous. This general equation is $c\gamma^2/1 - \gamma = K + D(c\gamma)^m$. Since $\gamma = \Lambda/\Lambda_0$ and the value of Λ_0 must also be selected to fit the data, this is a four constant equation.

An equation having a different form, but mathematically equivalent to the above equation, has been proposed independently by MacDougall.³

The argument of Kraus and Bray is based mainly on a discussion of data on non-aqueous solutions. They have applied their equation to a single aqueous solution, namely, potassium chloride, at 18°, using the data of Kohlrausch and Maltby. They reach the conclusion that the equivalent conductance of potassium chloride at infinite dilution at 18° is 128.3 instead of 130.1, which is the value given by Noyes' method and has been commonly accepted. Kraus and Bray's method thus gives a result which is nearly 1.5% lower than Noyes' method in this case. The method of Kraus and Bray requires a knowledge of the conductivity and viscosity of very concentrated solutions (up to several times normal). These data are not available in very many cases. They find it necessary to reject the data for solutions below 0.001 *N*, which by their method of plotting do not fall on the same curves as the data for all the stronger solutions.⁴ They conclude that these data are in error owing to the uncertainty in applying the water correction. Bates,⁵ on the other hand, lays especial

¹ S. J. Bates, *THIS JOURNAL*, **35**, 519 (1913).

² C. A. Kraus and W. C. Bray, *Ibid.*, **35**, 1315 (1913).

³ F. H. MacDougall, *Ibid.*, **34**, 855 (1912). MacDougall considers this a three constant equation, and assumes γ known, apparently overlooking the fact that Λ_0 must be selected to fit the data, and does not use the equation as a means of determining Λ_0 .

James Kendall, *Proc. Chem. Soc.*, **28**, 255 (1912), has proposed the equation $c\gamma^2/1 - \gamma = K + D(1 - \gamma/\gamma)$ which he derives theoretically from very improbable assumptions. He does not publish any attempts to test his equation by means of the available data. We have, however, convinced ourselves that it is not possible to find a value for Λ_0 which will make this equation agree with Kohlrausch's data on potassium chloride at 18°, and this equation therefore is not generally applicable.

⁴ Kraus and Bray, *Loc. cit.*, p. 1413.

⁵ Bates, *Ibid.*, p. 528.

emphasis on the data for these extremely dilute solutions. He says, "If these constants (equivalent conductances at infinite dilution) are to be known with a certainty greater than 0.1% it is necessary that accurate conductivity data be determined for solutions more dilute than 0.0001 *N*."

It is evident that a definite solution of this problem must await the collection and publication of much new data on the conductivity of both very dilute and very concentrated solutions and the viscosity of the latter. Pending the collection of the new data and the reinterpretation of the best of the old, and the general adoption of some new method of extrapolating to infinite dilution, it has seemed best to use the Noyes method in interpreting our data. Our results will then be consistent and comparable with the great body of figures in the literature dealing with ionic mobilities and ionization including the similar work of Bray and MacKay at 25°. The results calculated in this way will be equally useful for the calculation of the corrections to the electromotive force of our silver-silver iodide-iodine cells, because we do not need to know the absolute values of the concentration and mobilities of the ions in potassium iodide solutions and in potassium iodide solutions saturated with iodine, provided the ratios of these quantities are correct. We will, therefore, adopt provisionally the value 83.5 for the equivalent conductivity of potassium iodide at infinite dilution at 0°. Noyes and Falk¹ have calculated the identical value for this constant, using Déguisne's² data on the temperature coefficient of conductance. Déguisne's thesis does not give the actual conductance measurements but only the temperature coefficients. The most probable value of the equivalent conductance of the potassium ion appears to be 40.1. This is derived from the equivalent conductance³ of potassium chloride at infinite dilution at 0°, 81.4, and the transference number⁴ of the cation in this salt at 0°, 0.493. The equivalent conductance of the iodide ion at 0° is, therefore, $83.5 - 40.1 = 43.4$.

Referring again to Table III, Column 4 gives the degree of dissociation calculated by the usual formula $\gamma = \Lambda_c/\Lambda_0$. But since the viscosity of the more concentrated solutions is appreciably different from that of water, it will doubtless be more accurate to write $\gamma = \Lambda_c\eta/\Lambda_0\eta_0$, where η/η_0 is the relative viscosity of the solution to that of water at the same temperature, the results being given in Col. 5. Col. 6 gives $\Lambda_c\eta/\eta_0$, which is the conductivity to be expected in a solution of unit viscosity. This figure, from which viscosity effects have been eliminated, is a convenient figure to use in studying change in conductivity caused by adding iodine.

¹ Noyes and Falk, *THIS JOURNAL*, **34**, 468 (1912).

² Déguisne, Dissertation, Strassburg (1895); Landolt-Börnstein Tabellen, 1912 ed., p. 1116.

³ A. A. Noyes and K. G. Falk, *THIS JOURNAL*, **34**, 468 (1912).

⁴ *Ibid.*, **33**, 1454 (1911).

The Equivalent Conductance of Potassium Triiodide at 0°.

The experimental data concerning potassium iodide solutions saturated with iodine is also summarized in Table III, corrected to even concentrations, and a number of quantities calculated from the experimental data.

When iodine dissolves in potassium iodide, the volume of the solution increases and a correction must be applied, in the case of the stronger solutions, in order to compare them with the solutions of potassium iodide from which they were made. The change in concentration due to this volume increase was calculated for the stronger solutions, using our data for the density and concentration of these solutions. The concentrations expressed in terms of the total potassium salts ($KI + KI_3$) = ΣK in the solutions saturated with iodine are given in Col. 12.

Col. 13 gives the free iodine in the solution, that is, the total amount titrated with the arsenite solution. This includes free iodine dissolved in the water as I_2 and the iodine in the complexes ($I_3^- + KI_3$ and higher complexes if present).

The solubility of iodine in pure water was determined to be 0.000638 mols I_2 per liter (see page 256). Subtracting this amount from the total iodine gives $\Sigma I_3 = I_3^- + KI_3$ (assuming higher complexes absent).

Subtracting ΣI_3 from ΣK gives $\Sigma I = (I + KI)$ (Col. 15) the concentration of the iodide in the solution. In Col. 16, the ratio $\Sigma I_3/\Sigma K = r$ is given. This ratio is independent of the degree of dissociation, since it relates only to the total I_3 and total K .

The equivalent conductances of the solutions saturated with iodine are given in Col. 8. These equivalent conductances have been corrected for viscosity, and these corrected conductances are given in Col. 10.

The change in the equivalent conductance due to the solution of iodine to form the slower moving ion I_3^- is found by subtracting the data of Col. 10 from that of Col. 6. These differences are shown in Col. 11 ($\Delta\Delta$).

If we assume that, when part of the potassium iodide is converted into potassium triiodide, there is no change in the degree of dissociation of the remaining potassium iodide,¹ then the ratio $\Delta\Delta/r$ shown in the 17th column represents the decrease in equivalent conductance which would be

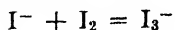
¹ This is in accord with what is known about the ionization of salts in mixtures.

"In a mixture of two salts with a common ion each salt has a degree of ionization equal to that which it has when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixture;" Arrhenius, *Z. physik. Chem.*, **2**, 285 (1888); Arrhenius, *Ibid.*, **31**, 218 (1899); MacGregor, McIntosh, Archibald and MacKay, *Trans. Nova Scotia Inst. Science*, **9** and **10** (1895-1899); A. A. Noyes, *Z. physik. Chem.*, **52**, 635 (1905); M. S. Sherrill, *THIS JOURNAL*, **32**, 741 (1910); G. M. J. MacKay, *Ibid.*, **33**, 308 (1911).

obtained if all of the iodide were changed into triiodide, and if the resulting triiodide had the same degree of dissociation that it has in the mixture. This does not involve the assumption that the degree of dissociation of potassium triiodide is identical with the degree of dissociation of potassium iodide. Subtracting this change of conductance from the equivalent conductance of potassium iodide solution gives the equivalent conductance of a solution of potassium triiodide of the concentration = ΣK , and having a degree of dissociation equal to the triiodide in the mixture. These data have been plotted in the same manner as the potassium iodide solutions, and the extrapolation made to infinite dilution. By this method the equivalent conductance of potassium triiodide at infinite dilution has been found to be 62.9. If the mobility of the potassium ion be taken as 40.1, that of the triiodide becomes 22.8.

The degree of dissociation of the triiodide is given in Column 19. On comparing this with the degree of dissociation of the potassium iodide corresponding, it will be noticed that the triiodide is slightly less dissociated below 0.02 *N* but in the 0.1 *N* and 0.05 *N* solution it is slightly more dissociated. The slightly smaller value for 0.001 *N* solution is probably not significant, since it is difficult to secure the same percentage accuracy in this dilute solution. Perhaps this exceptional behavior of the 0.1 *N* solution is only apparent and would disappear if the proper allowance could be made for the presence of higher complexes. The concentrations of the iodide and the triiodide ions and their ratio are given in the next three columns. This ratio is essentially constant for all the concentrations up to 0.05 *N* and 0.1 *N* and here falls off very slightly. This is somewhat remarkable in view of the previous work of Bray and MacKay at 25°. They found that at 25° the ratio I^-/I_3^- decreased from 1.14 to 0.99 with increasing concentrations from 0.001 to 0.1 *N* and became 0.35 at 1 *N*. No such marked deviation is found from the results of this investigation at 0°, although a slight tendency in that direction appears in the two stronger solutions. If this apparent deviation from the mass law at 25° is to be explained by the obvious assumption that a higher complex than KI_3 is formed, then the data at 0° would show that the formation of these higher complexes is much less at the lower temperature.

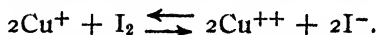
In the last column is shown the equilibrium constant for the reaction



obtained by multiplying the ratio of the preceding column by the solubility of iodine in water, 0.000638 mols per liter.

This equilibrium constant is slightly lower than that obtained by Fedotieff¹ in the study of the reaction,

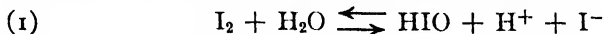
¹ Fedotieff, *Z. anorg. Chem.*, **69**, 31 (1911).



He obtained the constant 735×10^{-6} .

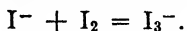
The Solubility and Hydrolysis of Iodine in Water at 0° .

In order to determine to what extent the reaction

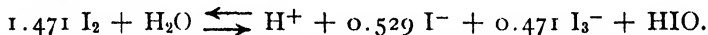


might interfere with the conductance measurements of the very dilute solutions, some pure water was saturated with iodine by shaking at 0° , and the conductance of the solution measured. The conductance of the water itself was measured after it had been shaken under the same conditions. The average of several determinations showed that the hydrolysis caused an increase of 0.6×10^{-6} mhos in the conductance. The solubility of the iodine was 0.0006383 mols per liter.¹

The reaction is further complicated by the side reaction



Combining the two equations, using the ratio $\Sigma\text{I}^-/\Sigma\text{I}_3^- = 1.125$ from Table III, gives



For every molecule of hydrogen ion produced, 1.471 mols of iodine are dissolved in forms other than I_2 . If the mobilities of the hydrogen, iodide, and triiodide ions are taken as 240, 43.4 and 22.8, respectively, then for the water solution assuming complete dissociation

$$\Lambda = 240 + 0.529 \times 43.4 + 0.471 \times 22.8 = 273.7$$

$$\text{and } c = \frac{\kappa \times 10^3}{\Lambda} = \frac{(0.6 \times 10^{-6}) \times 10^3}{273.7} = 2.2 \times 10^{-6} \text{ mols H}^+$$

produced. Since every mol of H^+ ion represents 1.471 mols of iodine, there are dissolved 3.2×10^{-6} mols of iodine in the form of HIO , I^- and I_3^- in the water. Subtracting this from the total solubility of iodine in water gives 0.0006380 mols I_2 dissolved.

The hydrolysis constant may now be calculated for reaction (1).

$$K = \frac{(\text{HIO})(\text{H}^+)(\text{I}^-)}{(\text{I}_2)} = \frac{(2.2)(2.2)(2.2 \times 0.53) \times 10^{-18}}{0.000638} = 9 \times 10^{-15}.$$

It is easy to show that hydrolysis is negligible in solutions containing $0.001 N$ KI. The iodide ion concentration in such a solution is 0.000514 and since $(\text{H}^+) = (\text{HIO})$ we have

$$9 \times 10^{-15} = \frac{(\text{H}^+)^2 \cdot 0.000514}{0.000638}$$

$$(\text{H}^+) = 1.05 \times 10^{-7}.$$

The increased conductivity is therefore

¹ This is lower than the value obtained by Fedotieff (*Z. anorg. Chem.*, **69**, 30 (1911), who obtained 1.30 mg. atoms per liter = 0.00065 mols per liter.

$$\frac{1.05 \times 10^{-7} \times 273.7}{1000} = 0.029 \times 10^{-6}$$

which is less than the uncertainty in the water correction and entirely negligible. The increase in free iodine dissolved in the form of HIO and I_3 owing to hydrolysis is 1.05×10^{-7} mols HIO and $0.471 \times 1.05 \times 10^{-7}$ mols I_3 together equivalent to 1.6×10^{-7} mols I_2 , which is also negligible.

It is a well-known fact that chlorine water liberates free oxygen, especially in sunlight, and therefore the possibility of a similar reaction occurring with the much weaker oxidizing agent, iodine, was considered. On the other hand, strong potassium iodide solutions when exposed to air and sunlight liberate free iodine. We must, therefore, consider the possibility of the reaction $2I_2 + 2H_2O \rightleftharpoons 4H^+ + 4I^- + O_2$. There are no electromotive data which throw light on this question at 0°. A study of the available data on iodine and oxygen electrodes at 25° indicates that under the conditions existing in a water solution of iodine there is a very slight tendency (about 0.04 volts) for oxygen to be liberated. This, however, gives no indication of the velocity of the reaction.

Another conceivable reaction is $3I_2 + 3H_2O \rightleftharpoons 6H^+ + 5I^- + IO_3^-$. Since the conductance of water was only increased by 0.6×10^{-6} mhos by saturation with iodine, it is obvious that none of these reactions can occur sufficiently to cause an appreciable error in our results. We have assumed that the increased conductance is caused by the reaction $I_2 + H_2O \rightleftharpoons HIO + H^+ + I^-$, as seems most probable. It is evident that none of these reactions occurs to an extent great enough to influence appreciably either the conductivity of our solutions or the amount of iodine dissolved. Therefore, it did not seem necessary to carry out experiments to decide between these alternatives.

A Comparison of the Results at 0° with those of Bray and MacKay at 25°.

The influence of the viscosity on the results having been found to be considerable at 0°, it seemed to us important to determine how great this influence is at 25°, and, if necessary, correct the results of Bray and MacKay.

The viscosities of a 0.1 *N* and 0.05 *N* solution of potassium iodide and the same solutions after saturating with iodine were found at 25° with the help of G. Y. Williams, the results being shown in Cols. 5 and 9 of Table IV.

The viscosities of the weaker solutions were obtained by interpolation. These results have been used to correct the results of Bray and MacKay, the results being shown in Table IV. The weaker solutions are, of course, not influenced by this correction, but it seemed worth while to reprint the figures in order to facilitate a comparison of the results at 0° and at

25°. Col. 7 shows that the degree of dissociation of potassium iodide is greater at 0° than at 25°. Bray and MacKay found the same effect of temperature on comparing their results at 25° with those of Kohlrausch at 18°. The influence of temperature on the dissociation of KI₃, on the other hand, although slight, is in the opposite direction. The solubility of iodine in potassium iodide solutions is somewhat less at 0° than at 25° (Cols. 13 and 14).

The most interesting comparison is found in Cols. 16, 22 and 23, which show a much greater constancy at 0° than at 25°. It is evident that the results conform to the requirements of the mass law much better at 0° than at 25°.

There is a slight deviation in the results at 0° with the two strongest solutions in the same direction as at 25°, but the deviations are comparatively small. The deviation from the mass law at 25° is discussed in considerable detail by Bray and MacKay, who reach the conclusion that the "activity of the ions is not proportional to their concentration."

Summary.

1. The conductances at 0° of potassium iodide solutions and of the same solutions saturated with iodine between 0.1 and 0.001 *N* have been measured.
2. The solubility of iodine in each of the solutions and in pure water has been determined.
3. The degree of dissociation of potassium iodide at 0° and 25° have been corrected for the change of viscosity of the solution.
4. The mobilities of the iodide and triiodide ions were found to be 43.4 and 22.8, respectively, at 0°.
5. The hydrolysis constant of iodine in water at 0° was found to be 9×10^{-15} .
6. The increase of the mass-law constant of the reaction $I_2 + I^- \rightleftharpoons I_3^-$ with the concentration of the solutions, which was found by Bray and MacKay at 25°, we now find at 0°.

HARVARD UNIVERSITY,
CAMBRIDGE, MASS.

ON THE ASSOCIATION OF MERCURIC CHLORIDE IN WATER SOLUTION.

By G. A. LINHART.

Received December 7, 1914.

It is a generally accepted fact that mercuric chloride in solution of a pure indifferent solvent does not associate.¹ The data thus far published are the results obtained from a study of the molecular weight of mercuric chloride in several organic solvents,² and seem to justify the above con-

¹ Abegg's *Handbuch der Anorg. Chem.*, II, 2, 615.

² Castro, *Gazz. chim. ital.*, 28, II, 317; Salvadori, *Ibid.*, 26, I, 237.

clusion. The ebullioscopic data, however, relative to the molecular weight in water solution are wholly unsatisfactory, as no two sets of figures, not even of the same investigator, agree. Thus Beckmann¹ gives for the molecular weight of mercuric chloride 318 and 297, although the amounts of mercuric chloride used in each of these determinations differed only by about 2%. Again he gives 284 and 275 when the original amounts of mercuric chloride used differed only by about 0.4%. Finally he gives 342 as the molecular weight. The same is true of the work of Kahlenberg² and Landsberger³ on the same subject. Another striking example of this unusual behavior of mercuric chloride in water solution are the results obtained by Hantzsch and Vagt,⁴ and Morse⁵ from distribution ratio measurements of mercuric chloride between water and toluene.

In view of these obvious discrepancies and of others more involved⁶ the present work had been undertaken to discover, if possible, some general property of mercuric chloride in water solution, which would account for its peculiar behavior in the several cases cited above. It will be shown in this paper, both experimentally and theoretically, that the deviation in the molecular weight, as well as in the distribution ratio, is due to the presence in water solution of the double molecules of mercuric chloride to a considerable extent, and also that the degree of association varies with the concentration and temperature, and may be determined accurately by means of several physical-chemical methods.

From the work of Hantzsch and Vagt, as well as that of Morse, it is evident that the distribution ratio of mercuric chloride between water and toluene is not constant, but decreases with the dilution. As mercuric chloride exists in the form of simple molecules in organic non-aqueous indifferent solvents,⁴ this is exactly what would be expected, since only the simple molecules can then enter the toluene layer. It follows that the lower the concentration of the total mercuric chloride in the water phase, the lower will be the number of double molecules, Hg_2Cl_2 , and therefore the proportionately greater will be the number of simple molecules entering the toluene phase, thereby causing a gradual decrease in the distribution ratio of mercuric chloride between the water and toluene. That this is actually the case may be shown from a recalculation of the results of the authors mentioned above.⁷ A small correction, however,

¹ *Z. phys. Chem.*, **6**, 460 (1890).

² *J. Phys. Chem.*, **5**, 367 (1901).

³ *Z. anorg. Chem.*, **17**, 450 (1898).

⁴ *Z. phys. Chem.*, **38**, 735 (1901).

⁵ *Ibid.*, **41**, 709 (1902).

⁶ Sand and Breest, *Z. phys. Chem.*, **59**, 426 (1907); **60**, 237 (1907); Sherrill, *Z. Elektrochem.*, **9**, 549 (1903); *Z. phys. Chem.*, **43**, 705 (1903); **47**, 103 (1904).

⁷ See these in discussion of results.

had to be applied in order to make their results fit the theory developed in this paper, because these investigators analyzed the water phase only. This means that a 0.3% error (which is within experimental error in the use of the sulfide method) in the water phase would correspond to about 4% error in the toluene phase. In recalculating their results, therefore, the corrections were applied to the actual amounts of mercuric chloride found in the water phase (and these corrections were in all cases well within experimental error) and the difference between these and the total mercuric chloride was taken as the amount of mercuric chloride in the toluene phase. It might be stated here that the method developed in this work and described below makes it possible not only to remove every trace of mercuric chloride from the benzene or toluene but also aids greatly in the subsequent precipitation as mercuric sulfide by hydrogen sulfide.

In a recent investigation¹ of the complex salts that mercuric chloride forms with sodium chloride and barium chloride, respectively, it was found that in a saturated solution of either of the above salts a comparatively small amount of mercuric chloride does not exist as such, but is completely in the form of complexes, such as NaHgCl_3 , Na_2HgCl_4 , and BaHgCl_4 . Moreover, as these compounds have been found to be practically insoluble in benzene, the usefulness of this method of extracting the mercuric chloride from the benzene phase was at once apparent. Attention is also called to the fact that in order to establish the existence of the double molecules of mercuric chloride in water solution, the greatest possible degree of accuracy is required in carrying out the experiments, and the results obtained from the analyses of the benzene phase and not those of the water phase must be used in the calculation of the equilibrium constants of the simple and double molecules existing together in water solution. The amount of mercuric chloride in the water phase is found by difference.

Experimental Part.

Method of Procedure.—The desired amount of pure mercuric chloride was weighed out on a watch glass and washed into a calibrated 250 cc. flask by means of a funnel, sufficient water added to dissolve the mercuric chloride completely (which was hastened by frequent shaking) and the flask then placed in a thermostat. After the solution reached the temperature of the bath the flask was filled to the mark, was thoroughly shaken and then replaced in the thermostat. Of this solution 200 cc. were transferred by means of a calibrated pipet into a stout bottle of 500 cc. capacity provided with a ground glass stopper. 200 cc. of thiophene-free benzene, which was also at the temperature of the thermostat, were then added after which the glass stopper was carefully inserted and the bottle rendered airtight by pouring paraffin upon the depression be-

¹ The work on this subject will appear in a subsequent number of *THIS JOURNAL*.

tween the outer part of the stopper and the lip of the bottle. After the paraffin solidified and showed no air holes a piece of strong canvas strap, about two inches in width, was used in strapping the stopper to the neck of the bottle. (This precaution was found necessary, as the paraffin seal would sometimes soften and allow a perceptible amount of benzene to escape which could be noticed by its odor.) The bottles thus prepared were immersed up to the necks in a thermostat kept at constant tem-

CURVES REPRESENTING SOLUBILITIES OF MERCURIC CHLORIDE IN WATER AND BENZENE, RESPECTIVELY.

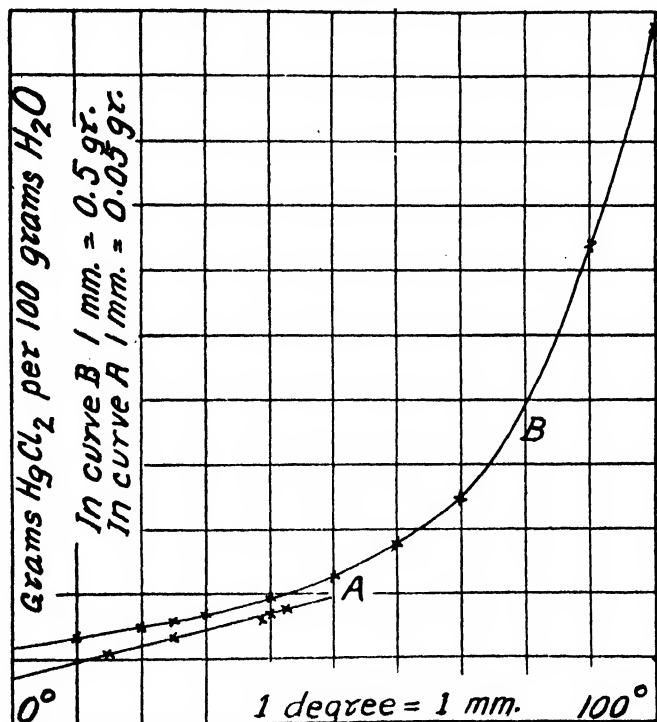


Fig. 1.

Curve A represents the solubility of mercuric chloride in benzene.
Curve B represents the solubility of mercuric chloride in water.

perature. Every two hours for about ten hours the bottles were thoroughly shaken and then allowed to remain over night in the thermostat. Each bottle was then in turn carefully removed, placed up to the neck in a glass vessel containing water of approximately the same temperature as that of the thermostat. (This precaution both in the filling and in the subsequent withdrawing of the solution was taken because of the uneven expansion of the two phases, since 200 cc. of water at room tem-

perature would expand to about 201 cc. at 40°, while 200 cc. of benzene would expand to about 204 cc. under like conditions.) After removing the strap and the paraffin seal the groove was carefully wiped with a piece

CURVES REPRESENTING THE DISTRIBUTION RATIOS OF MERCURIC CHLORIDE BETWEEN WATER AND BENZENE AND BETWEEN WATER AND TOLUENE.

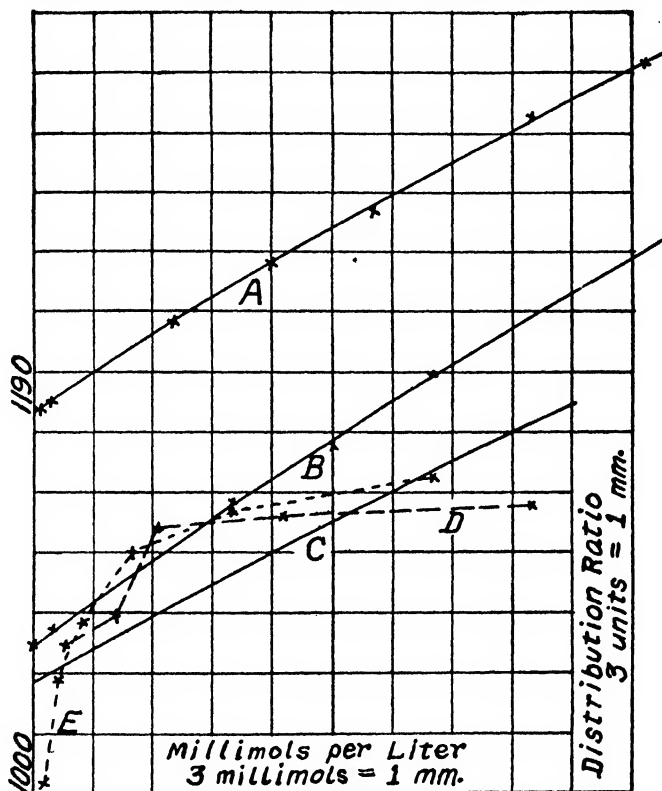


Fig. 2.

Curve A represents the slope of the distribution ratio at 25° of mercuric chloride between water and benzene.

Curve B represents the slope of the distribution ratio of mercuric chloride at 40° between water and benzene.

Curve C represents the slope of the calculated ratios of mercuric chloride between water and toluene at 25°.

Curve D represents the ratios given by Hantzsch and Vagt.

Curve E represents the ratios given by Morse.

Both of these curves (D and E) should coincide with C, which is the one theoretically calculated.

of filter paper, and the stopper gently tapped and removed without disturbing the two layers.

It has been found expedient in pipeting benzene not to apply suction,

but to blow the benzene into the pipet which was provided with a two-hole rubber stopper exactly fitting the glass bottle. Before inserting the pipet for the purpose of withdrawing the solution, the rubber stopper was so adjusted that the end of the pipet reached within about $\frac{1}{2}$ inch of the lower layer, in order not to disturb it. Of the 200 cc. of the benzene layer about three-fourths were slowly and uninterruptedly blown into the pipet to some distance above the 150 cc. mark, the upper end of the pipet stopped with the finger, the pipet slowly removed with the rubber stopper on it, and after allowing the benzene to flow down to the mark it was run into a 500 cc. separatory funnel. (The pipet was, of course, thoroughly rinsed with pure benzene after each operation, allowed to drain and then dried by means of a current of air.) 100 cc. of a clear saturated sodium chloride solution were then added, and the funnel vigorously shaken and finally allowed to remain at rest until the boundary line between the two layers became sharp. The lower layer was then run out into a 500 cc. beaker and the treatment of the benzene repeated with another 100 cc. of the clear saturated sodium chloride solution. Two treatments were found sufficient in most cases to remove every trace of the mercuric chloride from the benzene. To these 200 cc. of the saturated sodium chloride solution in the beaker containing the mercuric chloride were added 150 cc. of hot distilled water and a few cubic centimeters of pure hydrochloric acid. A slow current of well washed hydrogen sulfide gas was then passed into the solution (care being taken to keep the beaker always covered, thereby excluding possible oxidation of the hydrogen sulfide to free sulfur) until the precipitate was completely settled and the supernatant liquid became perfectly clear. This supernatant liquid was then passed through an ignited and weighed perforated platinum crucible fitted with an asbestos mat, the precipitate washed several times by decantation with freshly prepared warm hydrogen sulfide water, the precipitate washed into the crucible and the washing continued until all traces of chlorides were removed. It is important to note that the precipitate in the crucible cakes and shrinks, due to the suction, and that the crevices thus formed allow the wash water to be sucked through without effectively washing the precipitate. It is therefore necessary to plaster over these crevices with the flattened end of a glass rod. Also if the proper precautions have been taken in the precipitation of the mercuric sulfide, as well as in the preparation of the hydrogen sulfide water, the washing of the precipitate need not be followed by carbon disulfide and must not be followed by pure water, which would cause the mercuric sulfide to go through the asbestos filter in the form of colloidal mercuric sulfide. The precipitate was then dried in an oven between 105° and 110° to constant weight, allowed to cool in a desiccator and finally weighed.

TABLE I.—EXPERIMENTAL RESULTS.

| A. | Cw°. | $\frac{3}{4}B$. | Cb. | Cw. | R. | C _{HgCl₂} . | C _{Hg₂Cl₄} . | (10) ⁴ K. |
|---------------------|-------|------------------|---------------------|----------------------|------------------------|---------------------------------|---|----------------------|
| 25° | | | | | | | | |
| ... | ... | ... | 21.000 ¹ | 286.600 ¹ | 13.65 | 249.900 | 18.350 | 2.94 |
| 13550.0 | 250.0 | 605.2 | 17.391 | 232.609 | 13.38 | 206.953 | 12.828 | 3.00 |
| 9214.0 | 170.0 | 425.4 | 12.224 | 157.776 | 12.91 | 145.478 | 6.149 | 2.91 |
| 6504.0 | 120.0 | 306.2 | 8.798 | 111.202 | 12.64 | 104.696 | 3.253 | 2.97 |
| 3794.0 | 70.0 | 182.5 | 5.244 | 64.756 | 12.35 | 62.404 | 1.176 | 3.02 |
| 433.6 | 8.0 | 21.5 | 0.6177 | 7.3823 | 11.95 | 7.3506 | 0.0159 | 2.94 |
| 216.8 | 4.0 | 10.8 | 0.310 | 3.690 | 11.90 | ... | ... | .. |
| 108.4 | 2.0 | 5.4 | 0.155 | 1.845 | 11.90 | ... | ... | .. |
| At extreme dilution | | | | | 11.90 = R _∞ | | | |
| 40° | | | | | | | | |
| ... | ... | ... | 26.470 ¹ | 346.000 ¹ | 13.07 | 284.023 | 30.989 | 3.84 |
| 10840.0 | 200.0 | 532.6 | 15.296 | 184.704 | 12.08 | 164.126 | 10.289 | 3.83 |
| 8130.0 | 150.0 | 409.7 | 11.774 | 138.226 | 11.74 | 126.335 | 5.946 | 3.73 |
| 5420.0 | 100.0 | 279.8 | 8.041 | 91.959 | 11.44 | 86.280 | 2.840 | 3.82 |
| 2710.0 | 50.0 | 144.1 | 4.140 | 45.860 | 11.08 | 44.422 | 0.720 | 3.65 |
| 542.0 | 10.0 | 29.5 | 0.847 | 9.153 | 10.81 | 9.088 | 0.032 | 3.87 |
| At extreme dilution | | | | | 10.73 = R _∞ | | | |

A denotes the number of milligrams of mercuric chloride per 200 cc. of water solution.

Cw° denotes the number of millimols of mercuric chloride per liter of water solution.

$\frac{3}{4}B$ denotes the milligrams of mercuric sulfide actually obtained from the analyses of $\frac{3}{4} \times 200 = 150$ cm³. of the benzene phase.

Cb denotes the number of millimols of mercuric chloride per liter of the benzene phase.

Cw° — Cb = Cw, denotes the number of millimols of mercuric chloride per liter of the water phase.

$$\frac{Cw}{Cb} = R \text{ denotes the distribution ratio.}$$

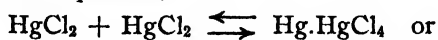
$$C_{\text{HgCl}_2} = R_{\infty} Cb$$

$$C_{\text{HgCl}_2} = \frac{Cw - R_{\infty} Cb}{2}$$

$$(10)^4 K = \frac{C_{\text{Hg}_2\text{Cl}_4}}{C_{\text{HgCl}_2}^2}$$

Discussion of the Results.

From the form of the equation,



$$K = \frac{C_{\text{Hg}_2\text{Cl}_4}}{C_{\text{HgCl}_2}^2} = \frac{1/2(Cw - CbR_{\infty})}{(CbR_{\infty})^2},$$

by means of which the equilibrium constants were calculated, it is evident that a knowledge of the true distribution ratio of the simple molecules, HgCl₂, between the water and the benzene (H₂O \longleftrightarrow HgCl₂ \longrightarrow C₆H₆)

¹ See calculations at the end of the article regarding these figures.

is very essential. This value may be found either by working with dilutions (4 and 2 millimols per liter, respectively) at which practically all the mercuric chloride is in the form of HgCl_2 , when the resulting distribution ratios become concordant; or, by plotting the several ratios obtained from the experiments at more convenient concentrations, and extending the line connecting these points to the coordinate representing zero concentration. In the experiments at 25° the former, or experi-

CURVES REPRESENTING THE ELEVATION OF THE BOILING POINTS.

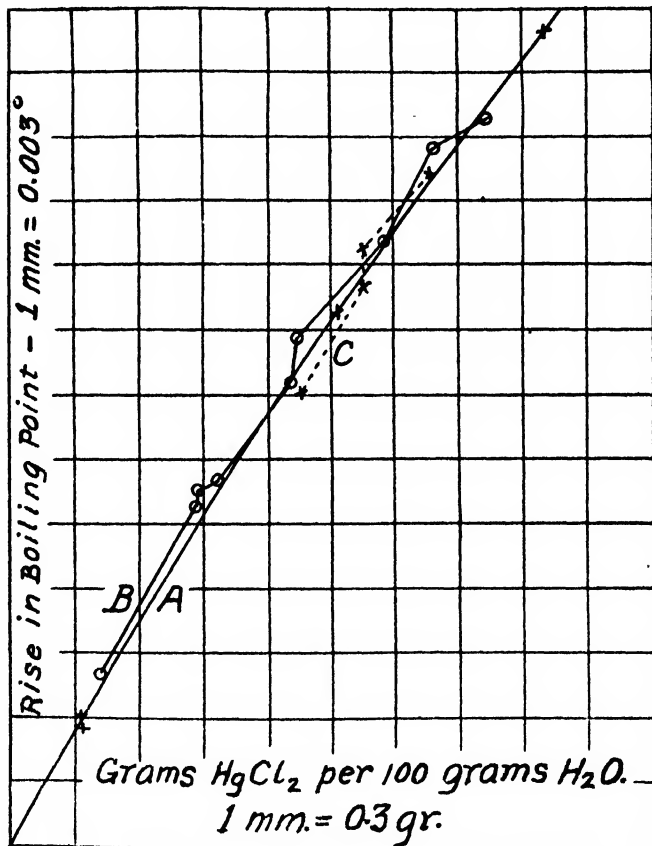


Fig. 3.

Curve A is obtained from the theoretically calculated values and practically coincides with the curve representing Kahlenberg's figures.

Curve B represents the values observed by Beckmann. It will be noticed that the 5th, 7th and 10th points lie close enough to the calculated line. These are the only ones that yield constants which are concordant with those of Kahlenberg, or those theoretically calculated.

Curve C represents the figures of Landsberger.

mental, method was used, while in the experiments at 40° the graphical method was applied.

It will be noted also that the distribution ratio is slightly lower at 40° than at 25° . This is due to the fact that the rate of solubility of mercuric chloride is proportionately greater in benzene than in water up to a certain temperature, as is shown by the relative positions of the curves representing the solubility of mercuric chloride in water and benzene, respectively. This decrease in the distribution ratio with rise in temperature is observed

CURVES REPRESENTING THE ASSOCIATION OF MERCURIC CHLORIDE AND THE EQUILIBRIUM CONSTANTS BETWEEN 0° AND 100° .

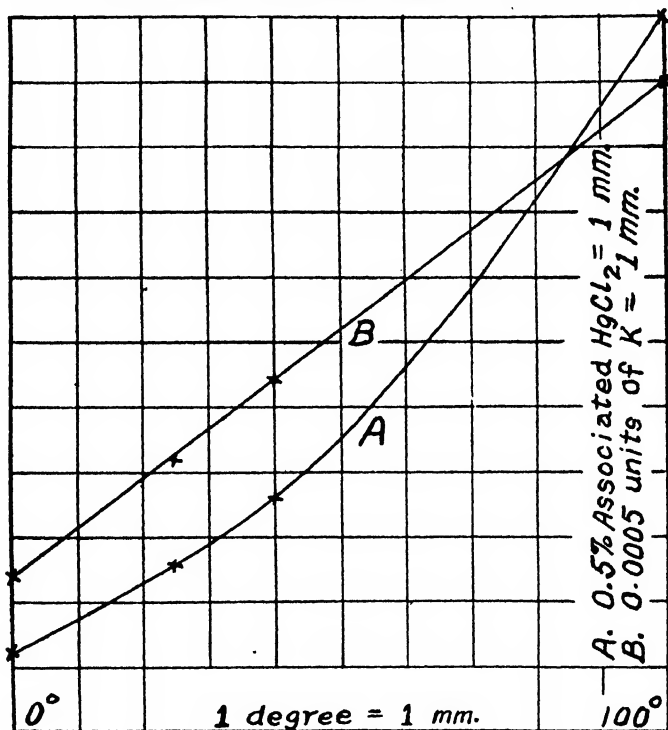


Fig. 4.

also in the results of similar experiments with toluene by Hantzsch and Vagt.¹

Finally, attention is called to the fact that K remains fairly constant from extreme dilution to saturation, which fact leads to the plausible conclusion that Hg_2Cl_4 is the only complex formed in pure water solution, for the given range of temperature, and possibly for any temperature between 0° and 100° as will be shown further on.

¹ *Z. phys. Chem.*, 38, 716 (1901).

TABLE II.—WORK OF OTHER INVESTIGATORS ON $\text{H}_2\text{O} \leftarrow \text{HgCl}_2 \rightarrow \text{C}_2\text{H}_5$.

| Calculated values. | | | | | | |
|--------------------|---------|--------|-------|-----------------------|--------------------------------|-------------------------|
| Cw° . | Cw . | Cl . | R . | C_{HgCl_2} . | $C_{\text{Hg}_2\text{Cl}_4}$. | (10) ⁴ K . |
| 250.0 | 230.544 | 19.456 | 11.85 | 205.261 | 12.642 | 3 |
| 125.0 | 114.782 | 10.218 | 11.23 | 107.800 | 3.491 | 3 |
| 62.5 | 57.248 | 5.252 | 10.90 | 55.409 | 0.919 | 3 |
| 31.2 | 28.540 | 2.660 | 10.73 | 28.063 | 0.238 | 3 |
| 15.6 | 14.2597 | 1.3403 | 10.64 | 14.140 | 0.060 | 3 |

 At extreme dilution $10.55 = R_\infty$

| Original data of Hantzsch and Vagt 25°. | | | | Cw calc. — Cw found. Correction in %. |
|---|--------|--------|-------|--|
| Cw° . | Cw . | Cl . | R . | |
| 250.0 | 229.9 | 20.1 | 11.44 | +0.28 |
| 125.0 | 114.9 | 10.1 | 11.38 | —0.10 |
| 62.5 | 57.4 | 5.1 | 11.32 | —0.26 |
| 31.2 | 28.6 | 2.6 | 10.88 | —0.21 |
| 15.6 | 14.3 | 1.3 | 10.73 | —0.28 |

—0.11 Av.

| Calculated values. | | | | | | |
|--------------------|---------|---------|-------|-----------------------|--------------------------------|-------------------------|
| Cw° . | Cw . | Cl . | R . | C_{HgCl_2} . | $C_{\text{Hg}_2\text{Cl}_4}$. | (10) ⁴ K . |
| 200.0 | 184.139 | 15.861 | 11.61 | 167.334 | 8.4025 | 3 |
| 100.0 | 91.737 | 8.263 | 11.10 | 87.175 | 2.2810 | 3 |
| 50.0 | 45.774 | 4.226 | 10.83 | 44.584 | 0.5950 | 3 |
| 25.0 | 22.862 | 2.138 | 10.69 | 22.556 | 0.1530 | 3 |
| 12.5 | 11.4245 | 1.0755 | 10.62 | 11.3465 | 0.0390 | 3 |
| 6.3 | 5.75626 | 0.54374 | 10.59 | 5.73646 | 0.0099 | 3 |

 At extreme dilution $10.55 = R_\infty$

| Original data of Morse 25°. | | | | Cw calc. — Cw found. Correction in %. |
|-----------------------------|--------|--------|-------|--|
| Cw° . | Cw . | Cl . | R . | |
| 200.0 | 184.10 | 15.90 | 11.58 | +0.08 |
| 100.0 | 91.93 | 8.07 | 11.39 | —0.18 |
| 50.0 | 45.90 | 4.10 | 11.20 | —0.27 |
| 25.0 | 22.89 | 2.11 | 10.85 | —0.12 |
| 12.5 | 11.42 | 1.08 | 10.57 | +0.04 |
| 6.3 | 5.73 | 0.57 | 10.05 | +0.45 |

0.00 Av.

Discussion of the Results of Hantzsch and Vagt, and of Morse.

It is evident from the experiments at 25° of Table I that the equilibrium constant K is equal approximately to 0.0003. Substituting this value of K and such value for R that would bring the necessary corrections within experimental error, in the equation

$$K = \frac{C_{\text{Hg}_2\text{Cl}_4}}{C_{\text{HgCl}_2}^2} = \frac{1/2(Cw^\circ - R_\infty Cl - Cl)}{(R_\infty Cl)^2}$$

We have,

$$Cl = -\frac{R_\infty + 1}{4R_\infty^2 K} \pm \sqrt{\frac{Cw^\circ}{2KR_\infty^2} + \left(\frac{R_\infty + 1}{4R_\infty^2 K}\right)^2}$$

The significance of the letters is the same as that of those in Table I, except that in place of *Cb* we have *Ct*. *Cw* may then be found by subtracting *Ct* from *Cw*^o. This procedure is legitimate, since these investigators analyzed the water phase only, although Morse claims to have analyzed the toluene phase also, by extracting the mercuric chloride from the toluene by means of water and subsequently evaporating the large volume of water solution of mercuric chloride, thus resulting to dryness. Realizing the unreliability of this method he has apparently not laid much stress upon the results thus obtained and has evidently made use of those found by the analysis of the water phase only, in the calculation of his results, which agree fairly well with those obtained by Hantzsch and Vagt.

TABLE III.

| Kahlenberg's original data. | | | Cal. from original data. | | |
|-----------------------------|-----------|-----------|--------------------------|-----------|-----------|
| <i>g.</i> | <i>D.</i> | <i>M.</i> | <i>i.</i> | <i>a.</i> | <i>K.</i> |
| 3.341 | 0.056 | 310.1 | 0.874 | 0.252 | (0.135) |
| 8.580 | 0.143 | 312.0 | 0.869 | 0.262 | 0.0567 |
| 15.463 | 0.248 | 324.2 | 0.836 | 0.328 | 0.0470 |
| 24.858 | 0.376 | 343.8 | 0.788 | 0.424 | 0.0514 |

0.0517 = Av.

Calculated values.

| | | | | | | <i>D</i> calc.— <i>D</i> obs. Correction in degrees. |
|---------------------|-------|-------|-------|--------------------|------|---|
| 3.341 | 0.060 | 289.4 | 0.936 | 0.127 | 0.05 | +0.004 |
| 8.580 | 0.144 | 308.8 | 0.877 | 0.245 | 0.05 | +0.001 |
| 15.463 | 0.247 | 326.1 | 0.831 | 0.338 | 0.05 | —0.001 |
| 24.858 | 0.377 | 343.0 | 0.790 | 0.420 | 0.05 | +0.001 |
| 53.965 ¹ | ... | ... | ... | 0.550 ¹ | 0.05 | ----- |

+0.001 = Av.

| Landsberger's original data. | | | Cal. from original data. | | |
|------------------------------|-----------|-----------|--------------------------|-----------|-----------|
| <i>g.</i> | <i>D.</i> | <i>M.</i> | <i>i.</i> | <i>a.</i> | <i>K.</i> |
| 13.54 | 0.210 | 335 | 0.810 | 0.38 | 0.073 |
| 16.53 | 0.259 | 332 | 0.820 | 0.36 | 0.053 |
| 16.54 | 0.277* | 311 | 0.870 | 0.26 | 0.030 |
| 19.70 | 0.312 | 329 | 0.850 | 0.30 | 0.042 |

0.049 = Av.

Calculated values.

| | | | | | | <i>D</i> calc.— <i>D</i> obs. Correction in degrees. |
|-------|-------|-------|-------|------|------|---|
| 13.54 | 0.218 | 322.6 | 0.840 | 0.32 | 0.05 | +0.008 |
| 16.53 | 0.262 | 328.5 | 0.825 | 0.35 | 0.05 | +0.003 |
| 16.54 | 0.262 | 328.5 | 0.825 | 0.35 | 0.05 | —0.015 |
| 19.70 | 0.306 | 334.6 | 0.810 | 0.38 | 0.05 | —0.006 |

—0.0025 = Av.

* Landsberger's extreme error 0.018.

¹ See discussion of results below under (b).

TABLE III (continued).

| Beckmann's original data. | | | Cal. from original data. | | |
|---------------------------|-----------|-----------|--------------------------|-----------|-----------|
| <i>g.</i> | <i>D.</i> | <i>M.</i> | <i>i.</i> | <i>a.</i> | <i>K.</i> |
| 4.35 | 0.080 | 283 | 0.957 | 0.085 | (0.024) |
| 8.68 | 0.159 | 284 | 0.954 | 0.091 | (0.012) |
| 8.72 | 0.165* | 275 | 0.985 | 0.029 | (0.004) |
| 9.75 | 0.170 | 298 | 0.909 | 0.181 | (0.027) |
| 13.16 | 0.215 | 318 | 0.852 | 0.296 | 0.047 |
| 13.42 | 0.235* | 297 | 0.912 | 0.176 | (0.019) |
| 17.60 | 0.281 | 326 | 0.831 | 0.338 | 0.045 |
| 19.93 | 0.325 | 319 | 0.849 | 0.301 | (0.031) |
| 22.22 | 0.338 | 342 | 0.792 | 0.416 | 0.056 |

0.049 = Av.

* Beckmann's extreme 0.006 and 0.020.

Calculated values.

D calc.—*D* obs.
Correction in degrees.

| | | | | | | |
|-------|-------|-------|-------|-------|------|--------|
| 4.35 | 0.077 | 293.6 | 0.923 | 0.154 | 0.05 | —0.003 |
| 8.68 | 0.146 | 309.0 | 0.877 | 0.246 | 0.05 | —0.013 |
| 8.72 | 0.147 | 309.4 | 0.876 | 0.247 | 0.05 | —0.018 |
| 9.75 | 0.162 | 312.2 | 0.868 | 0.264 | 0.05 | —0.008 |
| 13.16 | 0.213 | 320.7 | 0.845 | 0.310 | 0.05 | —0.002 |
| 13.42 | 0.217 | 321.9 | 0.842 | 0.315 | 0.05 | —0.018 |
| 17.60 | 0.277 | 330.5 | 0.820 | 0.360 | 0.05 | —0.004 |
| 19.93 | 0.309 | 335.0 | 0.809 | 0.381 | 0.05 | —0.016 |
| 22.22 | 0.341 | 338.8 | 0.800 | 0.400 | 0.05 | +0.003 |

—0.009 = Av.

Biltz's original data.

| Mols HgCl ₂ to 1000 g. H ₂ O. | Calculated from original data. | | | | |
|--|--------------------------------|-----------|-----------|-----------|-----------------|
| | <i>D.</i> | <i>g.</i> | <i>M.</i> | <i>i.</i> | <i>K.</i> |
| 0.01867 | 0.033 | 0.505957 | 283.64 | 0.9554 | 0.0891 (0.2122) |
| 0.04512 | 0.083 | 1.222752 | 272.54 | 0.9944 | 0.0112 0.0094 |
| 0.06464 | 0.118 | 1.751744 | 274.64 | 0.9868 | 0.0264 0.0159 |
| 0.09230 | 0.168 | 2.501330 | 275.43 | 0.9839 | 0.0322 0.0137 |

0.0130 = Av.

Calculated values.

D calc.—*D* obs.
Correction in degrees.

| <i>D.</i> | <i>g.</i> | <i>M.</i> | <i>i.</i> | <i>a.</i> | <i>K.</i> | |
|-----------|-------------------|-----------|-----------|---------------------|-----------|----------|
| 0.03443 | 0.505957 | 271.82 | 0.9970 | 0.0060 | 0.012 | +0.00143 |
| 0.08288 | 1.222752 | 272.94 | 0.9929 | 0.0143 | 0.012 | —0.00012 |
| 0.11830 | 1.751744 | 273.74 | 0.9900 | 0.0200 | 0.012 | +0.00039 |
| 0.16834 | 2.501330 | 274.88 | 0.9859 | 0.0283 | 0.012 | +0.00034 |
| ... | 5.73 ¹ | .. | .. | 0.0607 ¹ | 0.012 | |

+0.00050 = Av.

Observed *D.*Calculated *D.*

0.033

0.03443

0.083

0.08288

0.118

0.11830

0.168

0.16834

¹ See discussion of results below under (b).

Further evidence of the existence of the double molecule of mercuric chloride in water solution is shown by the ebullioscopic measurements of Kahlenberg, Landsberger and Beckmann,¹ and by the cryoscopic measurements of Biltz.²

Discussion of the Results of Kahlenberg, Landsberger, Beckmann and Biltz.

The equilibrium constants were first calculated from the original data, and then by means of the average of these constants the calculated values were obtained from the following well-known relations:

$$(1) K = \frac{a}{g(1-a)^2} \text{ or } a = \frac{2Kg + 1}{2Kg} \pm \sqrt{-1 + \left(\frac{2Kg + 1}{2Kg}\right)^2}$$

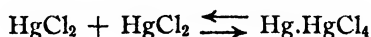
$$(2) a = \frac{1-i}{1-n} \text{ or } i = 1 - a(1-n)$$

$$(3) i = \frac{271}{M} \text{ or } M = \frac{271}{i}$$

$$(4) D = \frac{520g}{100M} \text{ in the ebullioscopic measurements}$$

$$\text{and } \frac{1850g}{100M} \text{ in the cryoscopic measurements,}$$

where g denotes the number of grams of mercuric chloride per 100 g. of water; D , the rise in the boiling point or lowering of the freezing point, as the case may be; M , the apparent molecular weight; i , the ratio of the true and apparent molecular weights; n , instead of denoting a whole number as in the case of substances which dissociate, equals $1/2$, because two molecules associate to form one; $100a$, the percentage of the mercuric chloride associated in the water solution; and K , the equilibrium constant of the equation:



$$\text{or, } K = \frac{C_{\text{Hg}_2\text{Cl}_4}}{C_{\text{HgCl}_2}^2} = \frac{ag}{(g-ag)^2} = \frac{a}{g(1-a)^2}$$

It is interesting to compare (a) the equilibrium constants obtained for the several temperatures 0° , 25° , 40° , and 100° , and (b) the percentage association in saturated solution of mercuric chloride in pure water at the given temperatures. For this purpose it is essential that the data from which the several constants were obtained be expressed in the same units; that is, the data must be expressed in millimols of mercuric chloride per liter, as in the distribution ratio measurements, or in grams of mercuric chloride to 100 g. of water, as in the ebullioscopic and cryoscopic experiments. The latter unit was chosen.

¹ *Loc. cit.*

² *Z. phys. Chem.*, 40, 199 (1902).

(a) From Table I we have at 25°, 286.6 millimols per liter corresponding to 7.9 g. of mercuric chloride per 100 g. of water; 18.35 millimols per liter of Hg_2Cl_4 corresponding to 1 g. of mercuric chloride per 100 g. of water. At 40° we have 346.0 millimols per liter of mercuric chloride corresponding to 9.62 g. of mercuric chloride per 100 g. of water, and 30.989 millimols per liter of Hg_2Cl_4 correspond to 1.7 g. of mercuric chloride per 100 g. of water.

Substituting these values in the equation:

$$K = \frac{ag}{(g - ag)^2}$$

and comparing the resulting constants with K for 100° and 0°, we have:

| | | | | |
|-----------|-------|-------|-------|-------|
| t | 0° | 25° | 40° | 100° |
| K | 0.012 | 0.021 | 0.027 | 0.050 |

If these four values of K are plotted on millimeter paper against their respective temperatures, the line formed by connecting the points is practically a straight line.

(b) Since the equilibrium constant K for 100° is equal to 0.050 and since the number of grams of mercuric chloride dissolved by 100 g. of water at 100° is equal to 53.965, we can calculate the percentages of association from the relation

$$K = \frac{ag}{g(g - ag)^2}$$

or, $100a = 55.00\%$ of the mercuric chloride associated at 100°. In a similar manner the percentages of the association of the mercuric chloride in saturated water solution at 40°, 25°, and 0° were calculated and tabulated together with the equilibrium constants for the corresponding temperatures.

| | | | | |
|---|-------|-------|-------|-------|
| t | 0° | 25° | 40° | 100° |
| K | 0.012 | 0.021 | 0.027 | 0.050 |
| % association of mercuric chloride in saturated water solution..... | 6.07 | 12.65 | 17.67 | 55.50 |

Summary and General Conclusions.

1. A method has been devised by means of which mercuric chloride may be removed from benzene quantitatively in a form very well adapted for the subsequent precipitation of the mercuric chloride by hydrogen sulfide.

2. By means of this method of analysis the proof of the existence of the double molecule of mercuric chloride in water solution was made possible by measuring the distribution ratio of mercuric chloride between water and benzene at 25° and at 40°, respectively.

3. The association of mercuric chloride in pure water is further established by the recalculated data of Morse, and Hantzsch and Vagt,

obtained from the measurements of the distribution ratio of mercuric chloride between water and toluene; of Biltz, obtained by cryoscopic measurements; and finally of Kahlenberg, Landsberger, and Beckmann, obtained by ebullioscopic measurements. Moreover, it is remarkable how closely the calculated values agree with those observed by the several investigators mentioned above. The differences between the calculated and the observed values are in every case well within experimental error, except in those of Beckmann; but even here the difference is lower than his own experimental error as is shown in the table.

4. From the fact that the equilibrium constants have been found to be fairly concordant from practically extreme dilution to saturation for a given temperature, it is reasonable to assume that Hg_2Cl_4 is the only complex in pure water at any temperature between 0° and 100° , and at any concentration.

5. It is interesting to note that the equilibrium constants from 0° to 100° all lie on practically a straight line, and also that the associated fraction of the mercuric chloride in the saturated water solutions between these temperatures, when plotted, lie on a perfectly smooth curve.

6. Finally it is hoped that by means of these equilibrium constants it may be possible to account for the many discrepancies and contradictory data given in the recent literature concerning the complex compound which mercuric salts form with other salts.

Method employed in this article of converting grams of mercuric chloride per 100 g. of water to millimols per liter of water solution and grams of mercuric chloride per 100 g. of benzene to millimols per liter of benzene solution and *vice versa*, by means of solubility and specific gravity data taken from the literature.

These figures were obtained from solubility data of mercuric chloride at 25° and 40° in water and benzene, respectively, by plotting on millimeter paper the number of grams of mercuric chloride per 100 g. of water against the temperatures, drawing a smooth curve along the points and reading off the figures (which are enclosed in parentheses in table) for any desired temperature accurately to three significant figures. The figures thus obtained were converted to millimols per liter of solution by means of specific gravity data as follows:

| GIVEN. | | | | | |
|------------|---|---|--|----------------------|---|
| $^\circ$. | Grams of HgCl_2 per 100 g. H_2O . ¹ | Grams of HgCl_2 per 100 g. C_6H_6 . ² | Sp. gr. of a 4.72% HgCl_2 water sol. ³ | Sp. gr. of water. | Sp. gr. of C_6H_6 . ⁴ |
| 0.0 | 5.73 | ... | 1.04070 | 0.99987 | ... |
| 10.0 | 6.57 | ... | 1.04033 | 0.99975 | ... |
| 15.0 | ... | 0.540 | ... | ... | ... |
| 20.0 | 7.39 | ... | 1.03856 | 0.99826 | ... |
| 25.0 | (7.90) | (0.652) | ... | 0.99712 | 0.87417 |

¹ Abegg's *Handbuch der Anorg. Chem.*, 2, II, 614.

² 0.540 was taken from Laszczynski; and 0.800 and 0.870 were taken from Linebarger, both of which are given in Landolt-Börnstein Tabellen, p. 593.

³ Abegg's *Handbuch der Anorg. Chem.*, 2, II, 615.

⁴ Beilstein, 2, 16.

GIVEN (*continued*).

| t° | Grams of HgCl_2 per 100 g. H_2O . | Grams of HgCl_2 per 100 g. C_6H_6 . | Sp. gr. of a 4.72% HgCl_2 water sol. | Sp. gr. of water. | Sp. gr. of C_6H_6 . |
|-------------|--|--|---|----------------------|--|
| 30.0 | 8.43 | ... | 1.03566 | 0.99577 | ... |
| 38.8 | ... | 0.800 | ... | ... | ... |
| 40.0 | 9.62 | (0.837) | ... | 0.99235 | 0.85829 |
| 40.5 | ... | 0.870 | ... | ... | ... |
| 50.0 | 11.34 | ... | ... | ... | ... |
| 60.0 | 13.86 | ... | ... | ... | ... |
| 70.0 | 17.29 | ... | ... | ... | ... |
| 80.0 | 24.30 | ... | ... | ... | ... |
| 90.0 | 37.05 | ... | ... | ... | ... |
| 100.00 | 53.96 | ... | ... | ... | ... |

FIND.

(a) The volume occupied by 1 g. of mercuric chloride, for example at 0° .

(b) Convert grams of mercuric chloride per 100 g. of water or benzene to millimols per liter of solution, at a given temperature.

(a)

From the table we have:

104.07 = the weight in grams of 100 cc. of solution, and (104.07), (0.0472) = 4.912 = weight in grams of HgCl_2 in 100 cc. of solution. $104.07 - 4.912 = 99.158$ = weight in grams of water in 100 cc. of solution. $\frac{99.158}{0.99987} = 99.171$ = volume in cc. of water in 100 cc. of solution. $100.000 - 99.171 = 0.829$ = volume in cc. of 4.912 g. of HgCl_2 in 100 cc. of solution. Hence, the volume occupied by 1 g. of mercuric chloride at $0^{\circ} = \frac{0.829}{4.912} = 0.169$ cc. In a similar manner were found the volumes occupied by 1 g. of mercuric chloride at 10° , 20° , and 30° , and the results tabulated below:

| t° | Volume occupied by 1 g. HgCl_2 . | Difference for 10° . | Average difference for 10° . |
|--------------|--|----------------------------------|--|
| 0° | 0.169 | ... | ... |
| | | 0.005 | |
| 10° | 0.174 | 0.004 | 0.005 |
| 20° | 0.178 | 0.007 | |
| 30° | 0.185 | | |

For the volume occupied by 1 g. of mercuric chloride at 25° , we may take the average of the volumes at 20° and at 30° , and the volume occupied by 1 g. of mercuric chloride at 40° we may find by adding the average difference 0.005 to the volume at 30° . Hence at 25° 1 g. of mercuric chloride occupies approximately 0.18 cc. and at 40° 0.19 cc.

Example: Conversion of solution at 40° of 9.62 g. of mercuric chloride per 100 g. of water to millimols per liter of solution:

$$\frac{100}{0.99235} = 100.771 \text{ cc. occupied by 100 g. of water}$$

$(9.62)(0.19) = 1.828$ cc. occupied by 9.62 g. of mercuric chloride. Total volume occupied by 100 g. of water and 9.62 g. of mercuric chloride = 102.6 cc. Therefore,

102.6 : 1000 = 9.62 : x or, x = 93.7622 g. of mercuric chloride per liter of solution, and

$\frac{93.7622}{0.271}$ = 346.0 millimols per liter of solution of mercuric chloride and water at 40°.

SEATTLE, WASHINGTON.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL.]

THE ELECTRON CONCEPTION OF VALENCE. VI. INORGANIC COMPOUNDS.

By J. M. NELSON AND K. GEORGE FALK.

Received October 22, 1914.

In the previous papers of this series,¹ the view that two atoms when combining acquire opposite electric charges was developed and applied to various classes of compounds and reactions.

In this paper, the electron conception of valence will be applied more especially to compounds and reactions of inorganic chemistry. The natural method of studying the present problem is to take the classifications developed by Werner and to consider them from the point of view of the electron conception of valence. It is manifestly impossible in a paper such as this, to take up all the relations Werner has developed. Instead, only some of the more important will be chosen, and the application of the electronic view to these, considered.

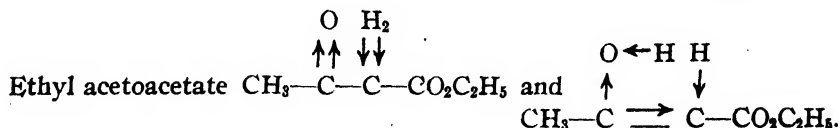
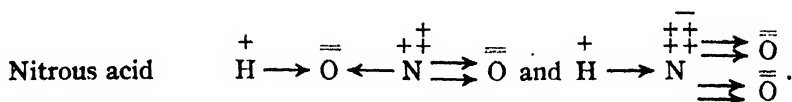
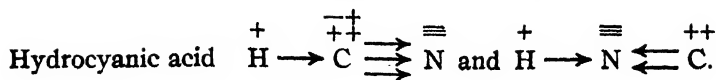
In discussing the structures of inorganic compounds, it is useful to consider many of them as tautomeric. The conception of tautomerism has been most useful in organic chemistry, where a number of tautomeric forms of various substances have been isolated and their chemical and physical properties studied. Tautomeric formulas have also been proposed for certain inorganic substances. Recently, Bray and Branch,² as well as Lewis,³ developed valence views from this standpoint in papers entitled "Valence and Tautomerism."

The application of the electron conception of valence to the phenomenon of tautomerism was outlined in previous papers. It was shown that the algebraic sum of the charges on each atom in a substance capable of existing in tautomeric forms remains the same in each of the forms, although the arrangement of the atoms may be different. This may be illustrated by the formulas for hydrocyanic acid, nitrous acid, and ethyl acetoacetate:

¹ *School of Mines Quarterly*, 30, 179 (1909); *THIS JOURNAL*, 32, 1637 (1910); 33, 1140 (1911); 35, 1810 (1913); 36, 209 (1914); *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 6, 212 (1912); *J. prakt. Chem., (N. F.)*, 88, 97 (1913); *Proc. Amer. Philosoph. Soc.*, 53, 25 (1914).

² *THIS JOURNAL*, 35, 1440 (1913).

³ *Ibid.*, 35, 1449 (1913).

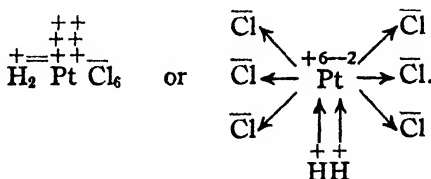


These formulas show that there is no oxidation or reduction reaction involved in the change of a tautomeric substance from one form to another. This is an important point in the further considerations.

Another fundamental relation is that which was described as onium compound formation and decomposition in a former paper,¹ and which involves the simultaneous loss and gain of a valence electron by one or more atoms of one or more molecules in a reaction. The formation of ammonium chloride from ammonia and hydrochloric acid according to

the equation² $\begin{array}{c} \equiv + \\ \text{NH}_3 \end{array} + \begin{array}{c} + - \\ \text{HCl} \end{array} = \begin{array}{c} \equiv \overline{++-} \\ \text{NH}_4\text{Cl} \end{array}$ in which the valence of the nitrogen is -3 in the one case and $-4 + 1 = -3$ in the other, is a simple example of this.

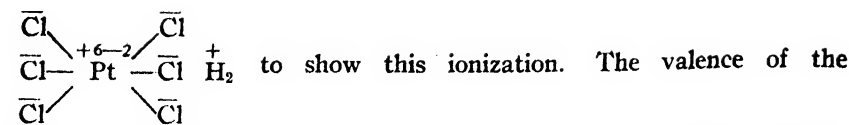
In beginning the study of inorganic compounds, it is advisable to consider a substance whose structure cannot be questioned. Platinic chloride must undoubtedly be represented by PtCl_4 . To pass from platinic chloride to chloroplatinic acid involves no oxidation or reduction of any of the atoms involved as far as can be told, and the latter may, therefore, be represented by the formula



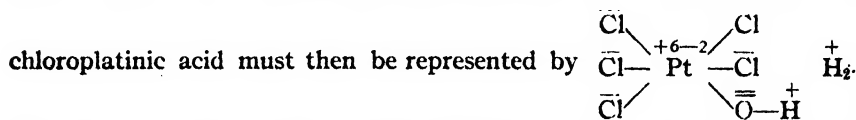
Chloroplatinic acid is a dibasic acid and may, therefore, also be written

¹ IV paper of this series, THIS JOURNAL, 35, 1810 (1913).

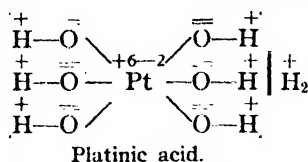
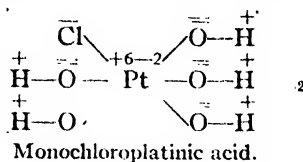
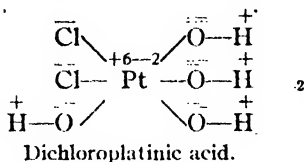
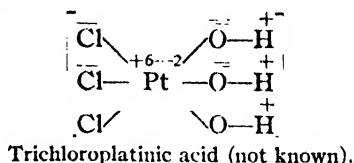
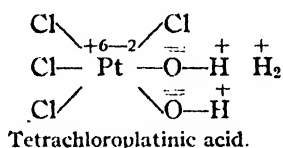
² This equation is probably not complete, as the presence of moisture is necessary for the reaction to proceed with finite velocity. It is possible, if the moisture acts purely catalytically, that this reaction would proceed as given although at a much smaller rate. In any event, the equation represents the change in the valence of the nitrogen atom to which it is desired to call attention in this connection.



platinum, or its state of oxidation, is $+6 - 2 = +4$ in chloroplatinic acid, just as it is in platinic chloride. The addition of hydrochloric acid to platinic chloride represents an onium compound formation. The negative chlorine combined with the positive platinum is not ionized, but the positive hydrogen combined with the positive platinum is ionized. The various chloroplatinic acids¹ may be considered next. In chloroplatinic acid, $\text{PtCl}_4 \cdot 2\text{HCl}$, HCl may be replaced by H_2O . This substance, pentachloroplatinic acid, $\text{PtCl}_4 \cdot \text{HCl} \cdot \text{H}_2\text{O}$, is also a dibasic acid. Without considering at present the possible mechanism of the reactions involved, but only the final formulas themselves, the structure of pentachloroplatinic acid must be analogous to that of chloroplatinic acid, or H_2O plays a part similar to that played by HCl . The formula for penta-



By analogy and in complete accord with the experimental facts, the positively charged hydrogens combined with the positive platinum are ionized, while the negatively charged atoms or groups combined with the positive platinum are not ionized. The other acids of this group given by Werner may be formulated in the same way:



¹ Werner, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie," III Edition (1913), pp. 40-1.

The fact that these acids are all dibasic proves that the acidity is **not** connected with the hydrogen of the hydroxyl groups,¹ and by comparing the whole series from chloroplatinic acid to platinum acid it is evident that the ionizable hydrogens are those combined directly with the positive central atom, platinum in this case. The salts of these acids may be formulated similarly.

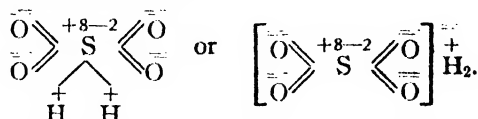
Platinum evidently is not capable of taking up in onium combination an unlimited number of positively and negatively charged atoms or groups. The compounds just considered show that the maximum number of positive charges that a platinum atom is able to receive (or negative atoms or groups that it can hold in direct combination) is six.² However, in compounds in which this maximum positive valence is shown, the platinum has also two negative electrons or valences with which it holds two positive atoms or groups. While six is the maximum number of positive charges that the platinum atom can hold, it does not in such compounds attain a higher state of oxidation than that represented by four positive charges.

Possibilities of tautomerism exist for these platinum acids but there is at present no experimental evidence that they have been realized. A consideration of these possibilities might obscure and confuse the main points which the discussion of the structures just given, is intended to bring out, so that it will not be given in this connection. Such possibilities will be considered later in connection with other substances.

It will be of interest to take up next a number of acids containing oxygen. Sulfuric acid will be chosen as a typical example. Its structure is formu-

lated ordinarily as $\begin{array}{c} \text{O} \\ \text{O} \end{array} \text{S} \begin{array}{c} \text{O} \\ \text{O} \end{array} \text{H} \begin{array}{c} \text{O} \\ \text{O} \end{array} \text{H}$. This structure is based upon a num-

ber of experimental facts, such as the reactions of organic derivatives of the acid and related compounds, the successive replacement of hydroxyl groups, etc. From the discussion of the platinum acids, it appears to be highly improbable for a substance with this formula to ionize as an acid. If, however, the structure is written in the tautomeric form, this difficulty disappears and sulfuric acid falls in line with the platinum acids. The tautomeric form of sulfuric acid is

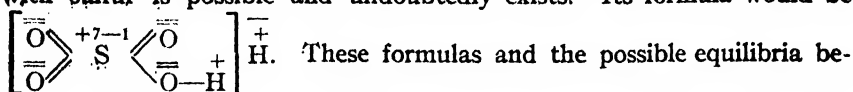


The positively charged ionizable hydrogen is in direct combination with the positive sulfur, while the negative oxygen (or hydroxyl in the first

¹ Werner, *Loc. cit.*, p. 32.

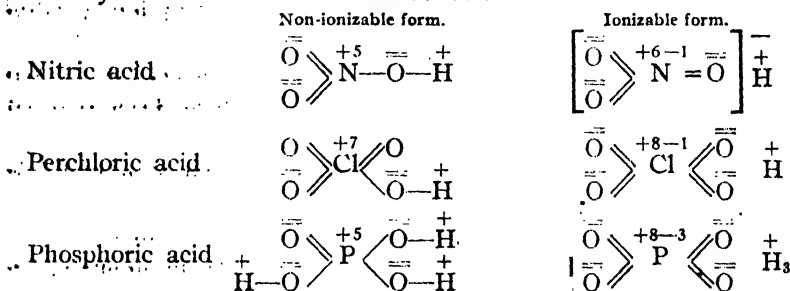
² The maximum coordination number of Werner, *Loc. cit.*, p. 52.

form) combined with the positive sulfur is not ionized. The state of oxidation of the sulfur atom is the same (+6) in both cases. An equilibrium unquestionably exists between the tautomeric forms of sulfuric acid. An intermediate form in which only one hydrogen is in direct combination with sulfur is possible and undoubtedly exists. Its formula would be



between the different tautomeric forms, together with the view that the hydrogen is ionized only when in direct combination with the central atom carrying a predominatingly positive charge, is suggestive in a number of directions. For instance, the anomalous behavior of strong electrolytes on ionization may, in part, be due to the existence of the tautomeric forms in solution and their different degrees of ionization.

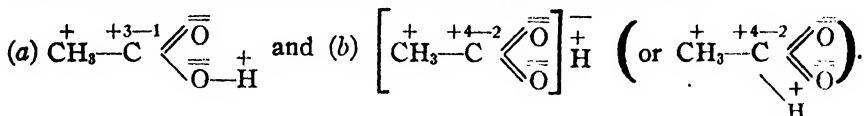
It is evident that all oxygen acids and salts may be considered in the same way. The formulas for some follow:



The number of oxygen atoms in combination with the central atom depends upon the specific chemical nature of that atom. In general, Werner points out¹ that four or six oxygen atoms held by the central atom represent the two common types of compounds of this nature. Considered from the electronic point of view, the central atom in these two types in the ionizable forms would possess eight or twelve positive charges due to the combination with the negatively charged atoms or groups, while the ionizable positively charged atoms or groups would give the central atoms a certain number of negative charges or corpuscles. The difference between the number of positive and of negative charges of these central atoms represent their state of oxidation. In nitric acid, the state of oxidation of the nitrogen atom is represented by five positive charges; of chlorine in perchloric acid by seven positive charges; of phosphorus in phosphoric acid by five positive charges, etc. With phosphoric acid, other intermediate tautomeric forms are possible and probably exist as indicated with sulfuric acid. Here, as there, the experimentally measured ionization may depend to a great extent upon the equilibria between the

¹ *Loc. cit.*, p. 121.

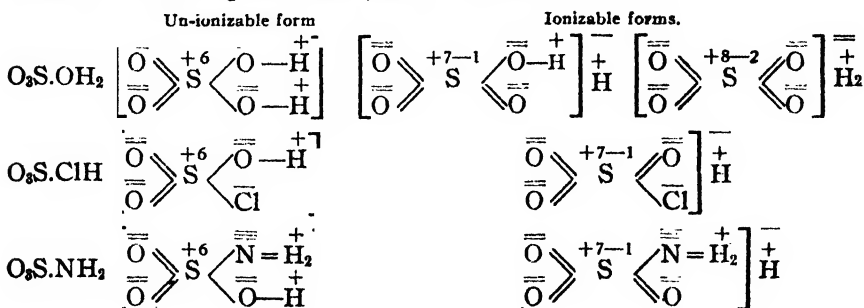
tautomeric ionizable and un-ionizable forms. This is brought out also by the organic acids which must belong to this group. With acetic acid; for instance, the tautomeric forms would be represented by



The *a* form represents the ordinary chemical non-ionizable form of acetic acid. *b* represents the ionizable form in which the carbon atom of the carboxyl group has both gained and lost an additional corpuscle and the substance exists in the tautomeric form. As far as known, carbon does not form such onium compounds readily, although as pointed out in previous papers such modes of combination must exist from indirect evidence,¹ so that the small degree of ionization of acetic acid, and, therefore, of most organic acids, may be due mainly if not entirely, to the conditions of the equilibrium, the un-ionizable form predominating greatly. With regard to the salts of organic acids, and evidently of all acids, it would appear that the conditions of the equilibria are somewhat different and that there the concentrations of the ionizable forms predominate.

In the preceding discussion, it might appear at first sight as if the difference between the tautomeric forms as postulated is the same as that assumed by Bray and Branch and by Lewis in their view of compounds with polar and nonpolar valences. From one point of view, the differences and explanations advanced are similar. From a broader point of view, considering not alone one set of phenomena but the general relations of the substances, the assumption of the existence of polar valences at one time and nonpolar valences at another, leads to contradictions, some of which were pointed out in the fifth paper.²

It may be of interest to formulate some of the compounds given by Werner,³ according to the present basis:



¹ IV paper, p. 1817.

² THIS JOURNAL, 36, 209 (1914).

³ *Loc. cit.*, pp. 30-1.

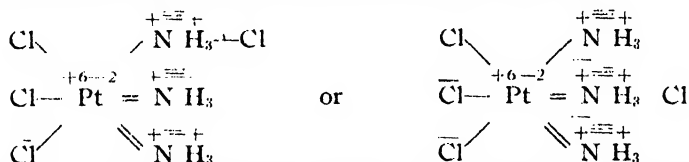
This un-ionizable form is in equilibrium with the ionizable form whose structure was given earlier. In this equilibrium, the ionizable form appears to predominate, but it is conceivable that the un-ionizable form might predominate in related compounds. All of the chloroplatinic acids might be formulated similarly, but since this would be only repetition, it will not be done here.

Platinic chloride, PtCl_4 , combines with 2 NH_3 to form a neutral un-ionizable substance.¹ In strict analogy with the tetrachloroplatinic acid

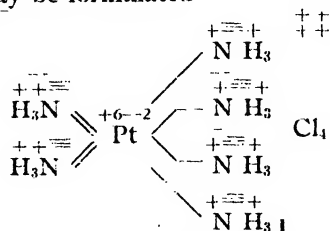
just given, this substance must be formulated $\text{Cl}_4^{+6-2} \text{Pt} \begin{cases} \text{N} \equiv \text{H}_3 \\ \text{N} \equiv \text{H}_3 \end{cases}$.

The platinum is in the same state of oxidation as before, while the nitrogen is combined with the platinum in the onium manner. The existence of tautomeric forms does not appear to be common with compounds of this type where ammonia is combined with a metallic element.

A third ammonia molecule may be introduced into tetrachlorodiammine platinum. In this way, trichlorotriammine platinum chloride is obtained, and ionizes into a negative chloride ion and complex positive ion. Since chlorine in direct combination with platinum is not ionized, it must follow that the ionized chlorine is in combination with nitrogen. On this basis, the following formula may be proposed for this compound:



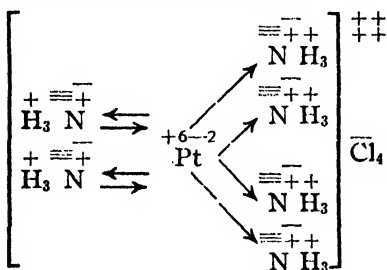
The state of oxidation of the platinum is unchanged. The negatively charged chlorine combined with positively charged platinum does not ionize, but when combined with negatively charged nitrogen it does ionize. This triammine salt is capable of taking up further molecules of ammonia. For each molecule of ammonia so added, a chlorine atom becomes ionizable, until finally with six ammonia molecules present in hexammine platinum chloride, all four chlorines may be present as ions. This last compound may be formulated



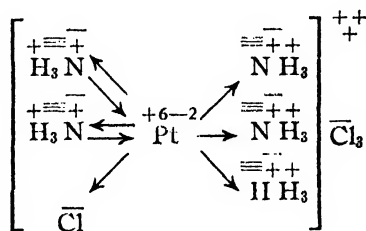
¹ Cf. Werner, *Loc. cit.*, p. 219, on the equivalence of water and ammonia as substituents.

If tautomerism were to take place with these compounds, the chlorine would be in combination with the platinum and would then not be ionizable. The reactions show that the form in which the chlorine is ionized predominates greatly in this equilibrium. The platinum atom throughout this series is neither oxidized nor reduced. The chlorine which ionizes is always in direct combination with negatively charged nitrogen.

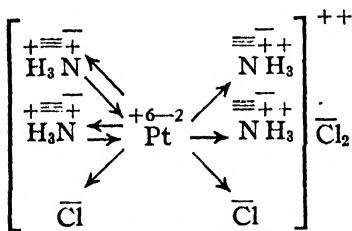
It may be of interest to formulate the complete series of platinum salts¹ in this connection. The formulas which are given represent the predominating forms present:



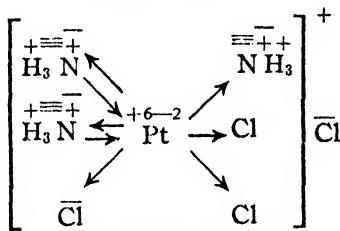
Hexammine platinum chloride.



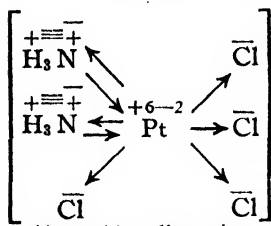
(Unknown.)



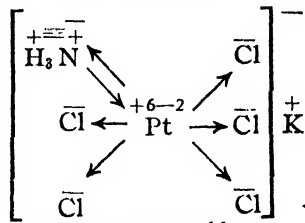
Dichlorotetrammine platinum chloride.



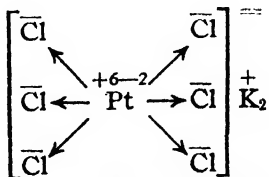
Trichlorotriammine platinum chloride.



Tetrachlorodiammine platinum.



Potassium pentachloroammine platinate.



Potassium chloroplatinate.

¹ Werner, *Loc. cit.*, p. 230.

In all of these compounds the valence of the platinum does not change but remains $+6 - 2$. The negative chloride ion is derived from the combination with negatively charged nitrogen in the onium form. Where chlorine is combined directly with positive platinum, it does not ionize. Where an ammonia molecule is combined directly with platinum with both valences forming onium linkings, no ionization appears. It is only when the nitrogen of the ammonia combines with one valence with the platinum and with the other with the chlorine to assume the onium form, that ionization of the chlorine takes place. It might perhaps be better to show in the formulas that the chloride ions in these complex platinum salts are derived from the ammonium part of the molecule and not from the platinum, but the symbolism introduced by Werner is so convenient that the formulas as given with all the charges indicated on the atoms may serve the purpose without creating confusion. The ionization of trichlorotriammine platinum chloride should follow the laws found experimentally for uni-univalent salts; of dichlorotetrammine platinum chloride, the laws for bi-univalent salts; and hexammine platinum chloride, the laws for tetra-univalent salts. The last two salts formulated above have a positively charged potassium atom in direct combination with positive platinum, and this potassium is ionized. These compounds have been discussed in sufficient detail before.

A summary of some of the relations just discussed may be of value here. The addition of ammonia to another molecule is due to its onium com-

$$\begin{array}{c} \cdot + - \quad + \equiv + - \\ \text{compound formation possibility. With } \text{HCl}, \text{H}_4 \text{N}^+ \text{Cl}^- \text{ is formed. With} \\ +6 = \quad + +7-1 \quad + \equiv + \\ \text{S O}_3, \text{ doubtless } \text{O}_3 \text{ S} \rightleftharpoons \text{N}^+ \text{H}_3 \text{ is first formed and then tautomerizes to the} \\ \text{better known } \text{O}_2 \text{ S} \begin{array}{l} \nearrow \text{OH}^+ \\ \searrow \text{NH}_2^+ \end{array} . \text{ With } \text{PtCl}_4, \text{Cl}_4 \equiv \text{Pt} \left(\begin{array}{c} +4 - - +6-2 \quad + \equiv + \\ \rightleftharpoons \text{N}^+ \text{H}_3 \end{array} \right)_2 \text{ is formed} \end{array}$$

and apparently does not tautomerize. Water plays an analogous part to ammonia,¹ and the relations may be formulated similarly. With

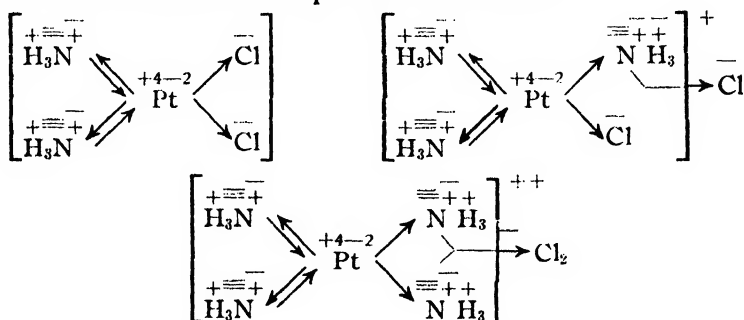
$$\begin{array}{c} + - \quad + - + - \\ \text{HCl}, \text{H}_3 \text{O}^+ \text{Cl}^- \text{ is formed. With } \text{S O}_3, \text{O}_3 \text{ S} \rightleftharpoons \text{O}^+ \text{H}_2 \text{ may be considered to} \\ +6 = \quad + +7-1 \quad + = + \\ \text{be formed first and then to tautomerize to the forms given before. With} \end{array}$$

$$\begin{array}{c} +4 - - +6-2 \quad + + + \\ \text{PtCl}_4, \text{Cl}_4 \equiv \text{Pt} \left(\begin{array}{c} \rightleftharpoons \text{O}^+ \text{H}_2 \end{array} \right) \text{ is formed first and then rearranges to the tauto-} \\ \text{meric ionizable form. These formulas appear natural for the compounds} \\ \text{with ammonia, but somewhat strange at first for the compounds with} \\ \text{water. Logically they must be grouped together, although in some cases} \end{array}$$

¹ Werner, *Loc. cit.*, pp. 257-64.

one set of phenomena predominates for one group in certain reactions and another set for another group in different reactions.¹

A brief comparison of the ammonia derivatives of platinous chloride, $PtCl_2$, with those of platinic chloride may be of interest. The series of platinous chloride ammonia compounds is as follows:²



In each of these compounds the platinum is in the same state of oxidation as in platinous chloride, +2. This differs in the state of oxidation from that of the platinum of $PtCl_4$, and it is only possible to pass from one series to the other by oxidizing or reducing the platinum.

The principles and relations developed for the complex platinum ammonia compounds may evidently be extended to any other compounds containing similar atoms or groups. Werner has given innumerable examples of these.

The relations of the complex ammonia salts are readily understood because the salt forming property of ammonia is so well known. If water were substituted for ammonia, similar classes and groups of compounds will be formed. The so-called basic properties of oxygen, or its ability to form onium compounds, are understood much better now than was the case relatively few years ago. If water were substituted for ammonia in $PtCl_4 \cdot 2NH_3$, the resulting compound $PtCl_4 \cdot 2H_2O$ tautomerizes and reacts as a dibasic acid as already explained. If water is substituted for ammonia in the platinum ammonia compounds containing more ammonia, then the water might act in the onium form just as the ammonia does. The negatively charged chlorine would then be combined with the oxygen of a water molecule, which is also combined with the platinum, and this negatively charged chlorine combined with negative oxygen would ionize. Whether such combination actually takes place with these compounds is questionable. It does, however, for such substances as hydrated

¹ It may be mentioned in this connection that the ordinary valence of the electronic point of view in which one corpuscle is transferred from one atom to another is analogous to the principal valence of Werner. The auxiliary valence of Werner corresponds in a number of compounds to the onium valence of the electronic treatment.

² Werner, *Loc. cit.*, p. 195.

nickel chloride, etc. The composition of the substance and the type of atoms in combination control the direction which is taken in these changes. These groups of substances include all those containing water of crystallization (or water of hydration in solution). If the water is held in onium combination, then the negatively charged element or group is combined directly with the negatively charged onium oxygen and is ionizable, while the positive ion will contain the atoms of the water molecule. Water or some similar substance must necessarily be present to bring about such ionization. This shows the importance of the solvent in ionization phenomena.

A brief discussion of the question of ionization may not be out of place here. From the considerations outlined in this paper, given in detail for a few typical substances but applicable in general, the following rule may be enunciated: *A positively charged atom ionizes only when in direct combination with an atom which contains a predominatingly positive charge; a negatively charged atom ionizes only when in direct combination with an* $+6-2+$ *atom which contains a predominatingly negative charge.* In Cl_6PtH_2 , negatively charged chlorine in direct combination with positive platinum does not ionize, but positively charged hydrogen in combination with platinum carrying $+6 - 2 = +4$ charges, ionizes. HCl in a solvent such as benzene does not ionize. In water, from the considerations ad-

vanced before (similar to those with ammonia), the compound $\text{H}_3\text{O}^+\text{Cl}^-$ is present.¹ The positively charged hydrogen combined with negative oxygen does not ionize, but negatively charged chlorine combined with oxygen carrying a predominatingly negative charge, ionizes. The ions here are $(\text{H}_3\text{O})^+$ and Cl^- .² With potassium hydroxide in water, the com-

compound formed would be $\begin{array}{c} \overset{+}{\text{K}} \searrow \quad \overset{+}{\text{H}} \nearrow \\ \quad \quad \quad \text{O} \\ \overset{+}{\text{H}} \nearrow \quad \quad \searrow \\ \quad \quad \quad \text{O} \end{array}$, and the ions $(\text{KH}_2\text{O})^+$

¹ A greater number of water molecules may be combined with the HCl, but the principle involved would be the same.

² The ionization of chloroplatinic acid and of hydrochloric acid indicates that hydrogen ions in aqueous solutions may be produced in two ways. With the former, the hydrogen ionizes directly, and after being separated, combines with and is in equilibrium with water and hydronium ions. With the latter, water combines first with the hydrogen chloride and then the hydronium ion is produced by ionization. In both cases, the final equilibrium between hydronium ion, hydrogen ion, and water, is the same; but the mechanism by which this equilibrium is attained is different in the two cases. The mechanism of the ionization of ammonium salts has not been taken up in this paper. However, it may be stated, that, since ammonia and water differ only in degree in onium compound formation properties, the explanation of the ionization of ammonium salts may be based upon reasoning similar to that given for the ionization of acids.

and $(\text{OH})^-$. The positively charged hydrogen and potassium combined with the negative oxygens are not ionized, while the negatively charged hydroxyl combined with the predominatingly negatively charged oxygen ionizes. These relations may be shown to hold generally. To go a step farther, and following Werner,¹ it may be stated that compounds of the first order do not ionize, but must go over into compounds of higher orders before ionization may appear.

An attempt is made in this paper to show the method by which the theoretical views of chemical structure based upon the classifications developed with the electron conception of valence may be used in connection with the classification based upon the relations founded on Werner's theory. It is manifestly impossible to enter into a systematic development in detail in a paper such as this. Instead, a few fundamental relations have been chosen and explained by means of typical compounds. A study of Werner's "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie" on the basis of these relationships will show a large number of applications and extensions of these views to related compounds. It is believed that the views developed here and explained in connection with Werner's classifications add certain ideas to the latter, and especially bring out, perhaps in ways not evident before, a connection between the valence structures of inorganic and organic compounds. As a first exposition of these views it is to be expected that uncertainties and questionable points with regard to individual compounds and perhaps to some of the generalizations will appear, but on the whole, the further development of the views outlined appears to promise useful classifications of the compounds of inorganic chemistry as a branch of chemistry in general.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A SEARCH FOR AN ALKALI ELEMENT OF HIGHER ATOMIC WEIGHT THAN CESIUM.

BY GREGORY PAUL BAXTER.

Received December 10, 1914.

Two years ago the writer was fortunate enough to secure a considerable quantity of pollucite, which was obtained in the Paris, Maine, region. The material contained, approximately, 33% of cesium, rubidium and potassium oxides, chiefly cesium oxide, besides about 2% of lithium and sodium oxides. Through the assistance of Mr. C. C. Wallace the bases were extracted from the mineral by fine grinding and digesting with concentrated nitric acid. Treatment of the silicic acid residue with hydrofluoric acid showed that the extraction with nitric acid was very nearly complete.

¹ *Loc. cit.*, p. 89.

The nitric acid extract was evaporated until a very considerable proportion of the cesium nitrate separated as such. From the mother liquor the aluminum was precipitated with an excess of ammonia. The filtrate was then evaporated to dryness, and the residue was freed from ammonium nitrate by ignition. The cesium nitrate was then purified further from sodium nitrate by two crystallizations. The final yield was somewhat over 3.5 kg. of fairly pure cesium nitrate.

With so large a quantity of this rare substance, it seemed well worth while to examine it carefully for the presence of an unknown alkali element of higher atomic weight, although Richards and Archibald¹ have already made such a search, unsuccessfully, with a much smaller quantity of material. Therefore, the whole quantity was subjected to a prolonged fractional crystallization of the nitrate according to the usual plan, since it seemed likely from the solubilities of the nitrates of the alkalis that the nitrate of any alkali metal of higher atomic weight than cesium would be the least soluble of all. After 18 series of crystallizations the least soluble fraction, which contained about 3 g. of cesium nitrate, and the extreme mother liquor, were carefully examined. The mother liquor, besides containing a very large proportion of sodium with much lithium, contained also rubidium, potassium and thallium.² Some of these elements may owe their origin in this material to the presence of a small quantity of lepidolite in the pollucite. The quantities of potassium, rubidium and thallium were, however, so small that they could not be detected spectroscopically in the original mineral.

The flame spectrum of the extreme crystal fraction was compared visually with that of one of the large intermediate fractions and no line could be seen in the spectrum of one which was not present also in that of the other. The spark spectrum of these fractions in the visible and ultraviolet regions also was examined by photography with a Féry quartz spectrograph, by placing the chloride between platinum electrodes. Here again, the spectrum was identical with that of one of the intermediate fractions.

Furthermore, the radio-activity of the least soluble fraction was investigated by means of a sensitive, gold-leaf electroscope, and the rate of discharge of the electroscope was found not to be accelerated in the least by the crystals. The same result was obtained with the original pollucite and with the residues obtained from the extreme mother liquor.

Finally the atomic weight of the least soluble fraction was determined through the chloride by Mr. O. J. Stewart.³ The nitrate was changed

¹ *Proc. Am. Acad.*, 38, 449 (1903).

² Both H. L. Wells and T. W. Richards found thallium as an impurity in cesium material. *Proc. Am. Acad.*, 38, 449 (1903).

³ Mr. Stewart carried out this experiment at the close of two years' continuous experience in the exact analysis of chlorides.

to chloride by several evaporations with an excess of hydrochloric acid in a quartz dish. Then the chloride was twice crystallized from a cold solution by saturating with hydrochloric acid gas, with centrifugal drainage of the crystals in each case. As the purified product weighed less than a gram, only one analysis was made. The salt was fused in an atmosphere of dry hydrochloric acid gas in a platinum boat contained in a quartz tube. It was bottled in the Richards "bottling apparatus" and its weight, in vacuum, was found to be 0.72285 g. After solution in water it was precipitated with an equivalent amount of silver, 0.46336 g. (in vacuum) of the latter substance being found to be necessary. When an excess of silver nitrate was added and the precipitate collected and weighed, 0.61583 g. (fused, in vacuum) of silver chloride was obtained. From the amount of silver necessary, the atomic weight of the specimen is computed to be 132.84 ($\text{Ag} = 107.880$; $\text{Cl} = 35.457$), while the silver chloride corresponds to an atomic weight of 132.79. The average result is 132.82, a value essentially identical with the value chosen by the International Committee upon Atomic Weights, 132.81, which depends chiefly upon the work of Richards and Archibald.

It is certainly obvious that the foregoing experiments give no indication of the existence of an unknown alkali element.

The generous assistance of the Carnegie Institution of Washington has facilitated the progress of this work in many ways.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY, YALE UNIVERSITY.]

A METHOD OF DETERMINING THE HYDRATES FORMED BY A SALT.

By H. W. FOOTE.

Received November 30, 1914.

It is a well-known fact that the addition of sulfuric acid in sufficient quantity to the saturated solution of a hydrated salt with which the acid does not react, will cause the salt to crystallize, either as a lower hydrate or in the anhydrous condition. As an illustration, Taboury¹ has shown recently that beryllium sulfate yields the dihydrate when crystallized from a solution containing two volumes of concentrated sulfuric acid, although the tetrahydrate is the form crystallizing from water. This property of producing a lower hydrate is not peculiar to sulfuric acid alone, for the same effect may be produced by dissolving any other substance, provided it is sufficiently soluble and does not react chemically. Van't Hoff² has shown, for instance, that magnesium sulfate crystallizes with only four molecules of water instead of with seven, in the presence of a

¹ *Compt. rend.*, **159**, 180 (1914).

² *Sitzungsber. K. Akad. Wiss. (Berlin)*, **1899**, 340.

saturated solution of magnesium chloride, and the similar dehydrating action of alcohol is well known. Sulfuric acid, however, has one advantage over many substances in producing this result, for it is miscible with water in all proportions, making it possible to reduce the concentration of the water to any desired extent. On the other hand, this acid, at least when concentrated, will react with the majority of salts so that the method is limited chiefly to sulfates.

It is possible, in certain cases, to use this means of preparing lower hydrates to determine all the stable hydrates which a normal sulfate can form at a given temperature. It is evident from the phase rule that the three-component system composed of water, sulfuric acid and sulfate is divariant when the three phases vapor, solution and (solid) hydrate are present, since the phases equal the components in number. At a given temperature, therefore, the hydrate can exist in contact with solutions which vary in composition within certain limits. When two hydrates are present, the system becomes univariant. As a result, at a fixed temperature, there will be but one solution, of definite composition, in equilibrium with the two solid phases and vapor. The proportions of the two solids may, however, be changed so that the composition of the solid residue, as a whole, may be varied while the composition of the solution has a fixed value. It follows that in a series of solubility determinations of a salt, with continually increasing amounts of sulfuric acid, the presence of a pure salt is shown by varying solubility and constant composition of residue, while constant solubility and variable residue show that two salts are present as a mechanical mixture. In this way, it is possible to detect all the stable hydrates of a normal sulfate which form at a given temperature. An exception occurs when an acid sulfate forms before the anhydrous sulfate.

The solubility results are comparable with the vapor pressures of the hydrates alone, without sulfuric acid or solution. At a given temperature, a pure hydrate can exist in contact with pressures of water vapor which vary within certain limits, just as it can exist in contact with solutions of varying concentration. A mixture of two hydrates, on the other hand, has a definite vapor pressure just as it has a definite solubility. The measurement of vapor pressures in the two-component system is one of the standard methods for detecting hydrates and has been used repeatedly. The solubility method, where it can be used, has some advantages over the other, for solubility determinations in general are much simpler to carry out than determinations of vapor pressure, and they are also more accurate. It has an equal advantage with the vapor-pressure method, in showing the range of conditions under which a given hydrate can form.

A number of investigations have been published on the solubility of

sulfates in varying concentrations of sulfuric acid, in which the composition of the solid phases has been determined, but these have usually been for the purpose of determining the acid sulfates. In the case of sodium sulfate¹ and of lithium sulfate,² each salt forms but one stable hydrate, and these appear on the solubility curves. Kenrick³ has determined the equilibrium in the system ferrous sulfate, sulfuric acid and water, but an acid sulfate appears before the anhydrous salt is obtained, so that equilibrium between the latter and the monohydrate does not exist in this system. Similarly, an acid sulfate of zirconium is formed immediately following the tetrahydrate, and lower hydrates and the anhydrous salt cannot be obtained by means of sulfuric acid.⁴ So far as I am aware, no case has been investigated in which a number of hydrates and the anhydrous salt can all be obtained by means of sulfuric acid. Copper sulfate forms

TABLE I.
Equilibrium in the System $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ at 25°.

| No. | Solution. | | Residue. | | |
|---------|----------------------|------------------------------|---------------------------|---|----------------------------------|
| | CuSO_4 , %. | H_2SO_4 , %. | H_2O , %. | Hydrate present. | H_2O , % (calc.) |
| 1..... | 18.47 | None | (36.04) ⁵ | 5 H_2O | 36.04 |
| 2..... | 12.62 | 11.14 | (36.04) ¹ | 5 H_2O | 36.04 |
| 3..... | 5.92 | 25.53 | (36.04) ¹ | 5 H_2O | 36.04 |
| 4..... | 3.25 | 36.77 | 36.12 | 5 H_2O | 36.04 |
| 5..... | 2.63 | 42.15 | 36.13 | 5 H_2O | 36.04 |
| 6..... | 2.59 | 47.66 | 36.05 | 5 H_2O | 36.04 |
| 7..... | 2.83 | 49.00 | 35.57 | 5 H_2O and 3 H_2O | ... |
| 8..... | 2.83 | 49.20 | 34.14 | 5 H_2O and 3 H_2O | ... |
| 9..... | 2.84 | 49.29 | 28.64 | 5 H_2O and 3 H_2O | ... |
| 10..... | 2.70 | 50.23 | 26.23 | 3 H_2O | 25.29 |
| 11..... | 2.19 | 54.78 | 25.35 | 3 H_2O | 25.29 |
| 12..... | 2.11 | 55.84 | 19.38 | 3 H_2O and 1 H_2O | ... |
| 13..... | 2.15 | 55.60 | 16.12 | 3 H_2O and 1 H_2O | ... |
| 14..... | 0.95 | 61.79 | 10.47 | H_2O | 10.14 |
| 15..... | 0.17 | 77.93 | 10.14 | H_2O | 10.14 |
| 16..... | 0.15 | 83.29 | 10.87 | H_2O | 10.14 |
| 17..... | 0.19 | 85.46 | 10.79 | H_2O | 10.14 |
| 18..... | 0.44 | 85.72 | 9.16 | H_2O and 0 H_2O | ... |
| 19..... | 0.42 | 85.81 | 7.64 | H_2O and 0 H_2O | ... |
| 20..... | 0.40 | 86.04 | 1.03 | Anhydrous | None |
| 21..... | 0.19 | 92.70 | 0.83 | Anhydrous | None |

¹ D'Ans, *Z. anorg. Chem.*, **49**, 356 (1906); **61**, 91 (1909).

² Van Dorp, *Z. physik. Chem.*, **73**, 289 (1910).

³ *J. Phys. Chem.*, **12**, 693 (1908).

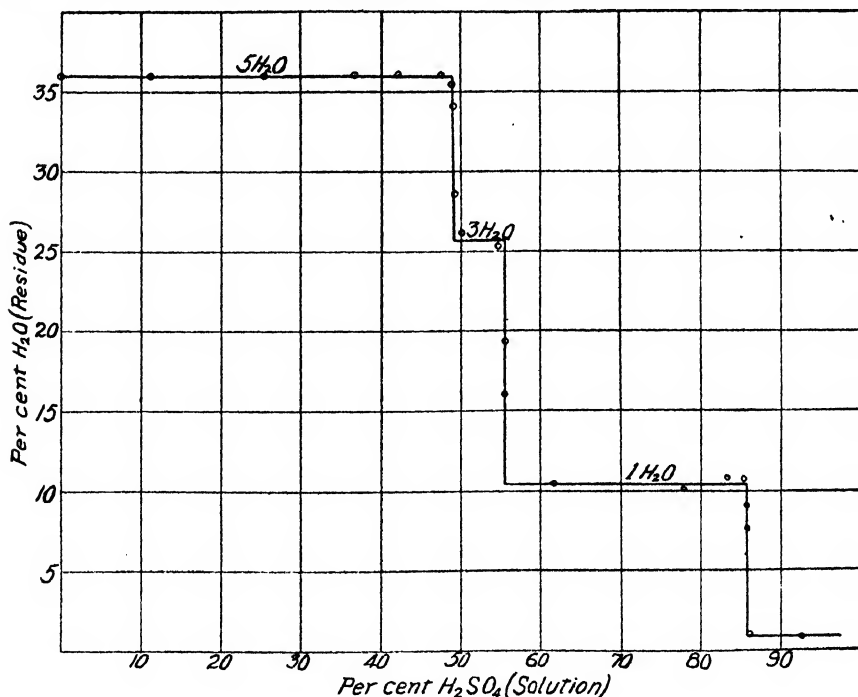
⁴ Hauser, *Z. anorg. Chem.*, **54**, 196 (1907).

⁵ These values were not determined directly and the calculated value for the pentahydrate is used.

three well-known hydrates and no acid salts interfere. It is, therefore, well suited to illustrate the relations mentioned.

A series of mixtures was prepared containing copper sulfate and water, with continually increasing proportions of sulfuric acid. The mixtures were heated, placed in glass-stoppered bottles sealed with paraffin, and rotated at 25° in a thermostat. No difficulty has been experienced, thus far, in reaching equilibrium after twenty-four hours. Samples for analysis were drawn off through a filter of glass wool. Copper was determined electrolytically and total sulfate by precipitating as barium sulfate. The proportions of copper sulfate and sulfuric acid could then be calculated. The residues were filtered on a filter plate covered with asbestos and washed with strong alcohol. Previous experience had shown that strong alcohol reacts very slowly with dehydrated salts which are insoluble in it. A small amount of acid, averaging less than 1%, always remained in the residue and causes an error in the water determination, giving somewhat high results. Chiefly for this reason, the analysis of the solutions is somewhat more accurate than that of the residues. The results obtained are given in Table I.

The results have been divided into groups in each of which either the solution or the residue remains constant in composition while the other varies. The percentage of copper sulfate falls off rapidly to rather low



values with increasing content of sulfuric acid so that the change in composition of solution is better illustrated by the results for sulfuric acid. In the figure, the results have been plotted. Ordinates represent percentage of water in the residue, and abscissas, the percentage of sulfuric acid in solution. This brings out clearly the range of conditions under which each hydrate forms, this being represented by the length of the horizontals. The conditions for the trihydrate are very narrow while the pentahydrate forms under the widest range, being stable in contact with solutions containing as much as 49% of sulfuric acid.

Solutions which are in equilibrium with two solid hydrates should have the same vapor pressure as that of the hydrates themselves.¹ The vapor pressure of the solutions in Nos. 7-9 of the table, for instance, should be equal to that of a mixture of the solid pentahydrate and trihydrate. Whether this way of determining the vapor pressures of hydrates will offer any advantage in accuracy or convenience has not yet been tested. Where the solubility of the salt is slight, as it is in the solution in equilibrium with anhydrous salt and monohydrate (Nos. 18-19), the vapor pressure of the solution is nearly that of the sulfuric acid solution alone.

I plan to extend this method to a number of sulfates which form more than one stable hydrate.

SHEFFIELD CHEMICAL LABORATORY,
YALE UNIVERSITY, NEW HAVEN, CONN.

ELECTRIC SYNTHESIS OF COLLOIDS.

By JNANENDRANATH MUKHOPĀDHYĀYA.

Received December 11, 1914.

The present work was undertaken with a view to elucidate the process of formation of sols by the electric method first utilized by Bredig² for the preparation of sols in water, and subsequently modified by Svedberg³ for obtaining sols in non-aqueous media and of various substances besides metals. Bredig's own method is now a general one and has been extended by others to media other than water.

Much difference of opinion exists as to the process of formation of the sol by these methods. Wo. Ostwald, and others,⁴ hold that the process is of an electro-chemical nature and the substance goes into the liquid in the atomic form, under electric forces and afterwards becomes aggregated. Benedicks⁵ and others lay stress on the thermal side of the process and are of the opinion that the metal partly volatilizes and partly

¹ Foote and Scholes, *THIS JOURNAL*, **33**, 1309 (1911).

² *Z. angew. Chem.*, **1898**, 951.

³ *Ber.*, **39**, 1703 (1906).

⁴ Cf. Ostwald's *Grundriss der Kolloid Chemie*.

⁵ *Z. Chem. Ind. Kolloide*, **11**, 263 (1912).

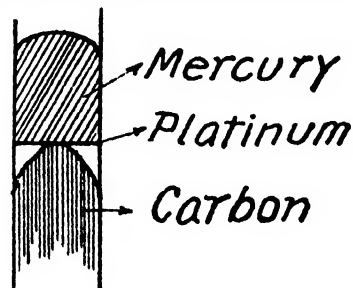
melts. Kutscheroff¹ has made experiments to prove his view of the process. He has studied the formation of sols using pairs of different metals as the two electrodes in Svedberg's method and has measured the amounts of the metals that pass into solution. He concludes that the metals go into the liquid as changed atoms, as shown by the fact that the ratio of the quantities of each passing into colloidal solution is the same as that of their equivalent weights. He, however, separates the coarse particles formed by the process by decantation and considers their formation to be due to a different process, possibly thermal, but adduces no reason for such assumption. His results show wide divergence from those of Svedberg. This divergence is due, possibly, to the uncertainty of the measurements, as we have to deal with small quantities of substances, and to Kutscheroff's arbitrary separation of the coarser particles.

Further, in cases of metals of variable valency, in calculating the ratio of the equivalent weights, in some cases he takes the metal to act with both valencies, sometimes with only one, thus acting quite arbitrarily, as pointed out by Benedicks. These considerations show that his data have not much significance.

Benedicks holds the view that the process of colloid formation is mainly of a thermal character and that the metal melts under the conditions into fine drops which remain suspended.

It seems possible that, under the intense heat of the powerful arcs produced in all these methods, the metal volatilizes and the surrounding liquid effects a sudden and rapid cooling and hence the vapor condenses to fine solid particles, resulting in a colloidal solution. Hence it was thought that if by any means the vapor of a substance which was solid at the ordinary temperature was produced in a liquid in which the substance was insoluble, a colloidal solution might be obtained.

To investigate the thermal effect it was decided to heat, under water, a substance which is insoluble in water. This was realized in the following way: The substance was finely powdered. A thin platinum wire was joined with two binding screws at the end of two stout copper wires clamped to two stands. These were in circuit with the adjustable resistance, two storage cells, an ammeter and a key. The platinum wire was thin enough to fuse with a current of 4 amps. in air. It was raised to a dull red heat by adjusting the resistance with a suitable current. The platinum wire was dipped in the pow-



Figure

¹ *Z. Chem. Ind. Kolloide*, **11**, 165 (1912).

dered substance, which melted and stuck to the wire. In this way, with a little care, a thin, uniform coating of the substance was obtained on the wire.

The coated wire was then placed in a beaker containing "conductivity" water just covering the binding screws at a temperature of about 2°.

A current of 15 amperes was then sent through the wire. This could be done without fusing the wire, as the surrounding cold water carries the heat very rapidly by convection. Very soon the liquid becomes colored and a sol is formed. Thus with sulfur a milky white coloration, which becomes deeper as the current continues, is obtained in five minutes. Sols of selenium and arsenic have also been obtained in this method. Arsenic shows a very fine cone when a beam of sunlight is passed through it (Tyndall phenomenon), but its yield is very small.

Certain organic substances, such as α -naphthol, benzophenone, dibenzyl, anthracene, etc., were treated in the above way and a sol-like formation was observed in most cases. But most of these substances are slightly soluble at a high temperature, so that on cooling an opalescence due to the separation of fine particles is visible. Hence no definite conclusion can be drawn from these observations.

The temperature to which the wire is raised in this way is, after all, not so high, so it was decided to utilize the intense heat of the carbon arc.

An arc between two carbon electrodes was struck under water with 220 volts and a current of 2 amperes. The electrodes were placed vertically one above the other. The lower one was coated with the substance in the following way: The substance was melted in a crucible and the carbon rod with a flat head was dipped into it and hence a thick coating was obtained. The centre of the coating was scooped out with a knife, forming a small hole exposing the carbon. The upper carbon electrode was rubbed to a point and was held just above the coated one so that the pointed end of the former was just above the hole exposing the carbon in the latter. On striking an arc, bubbles of water vapor rise with a hissing sound. These bubbles also carry with them vapors of the substance as shown by the fact that fine particles like little puffs of smoke with characteristic color come out and condense on the side of the beaker (or the vessel containing water and in which the arc is immersed) as small drops, if the depth of water above the arc be not too great. The outer layer of the bubbles condenses and in some cases forms a skin; when the bubble rises just above the surface, it breaks—the gas included within it goes away as a little puff of smoke.

In this way it is possible to obtain dispersions of S, Se, P, dibenzyl and β -naphthol.

When the arc is struck, the carbon electrodes become enormously heated. The distance between the two electrodes can be easily regulated so that

it is possible to strike an arc with one just above and very near the coating, which becomes very much heated and the processes described previously take place. By a little practice the arc can be struck in the desired way.

Non-conducting substances were chosen to exclude any possibility of their taking part in the arc. Most organic substances are decomposed, however, at the high temperature of the arc, so very few of them may be used. It seems that both sulfur and selenium decompose water at the high temperature; these colloidal solutions show slight acid taste.

Sulfur, selenium, and phosphorus give good results. The deposit of phosphorus on carbon was obtained with white phosphorus melted under hot water. The low melting point of phosphorus presents some difficulties; the deposit melts and falls off to the bottom of the vessel when the arc is struck; but by repeated treatment of the same sample, fair yields are obtained. Another inconvenience is that the whole of the substance vaporized cannot be condensed completely under water, as part of it passes off as a vapor and another part condenses as a thin skin on the side of the beaker. With a small current density the yield is better. Since the liquid becomes hot during the experiment, it is better to cool the water with a freezing mixture.

In all cases "conductivity" water was used. With previously cooled water and with a current of 0.6 ampere good results are obtained in the case of selenium. The selenium sol improves on standing; this may be attributed to the oxidation of H_2Se by the atmospheric oxygen. If a little dilute nitric acid is added the effect is instantaneous. The sol is of brown color and is fairly stable.

Generally, when the sol is just prepared and is not disturbed, the upper part of the vessel contains the concentrated sol with the deep brown color.

All of these sols show the Tyndall phenomenon, a homogeneous cone of light being visible in all cases and they are fairly stable. The cone breaks up and finally disappears on the addition of electrolytes (*e. g.*, ZnSO_4 , BaCl_2 , etc.).

Also some observations were carried out with cadmium, mercury and copper.

Cadmium.—A deposit of the metal was made as usual on one of the carbon electrodes with a small hole exposing the carbon.

If the arc strikes directly on the metal, a green color is visible, but if it strikes on the carbon no color is noticeable. Little puffs of smoke containing particles of cadmium come out as in the case of sulfur. The hot cadmium reacts with water and some hydroxide is formed from the metal.

This sol being unstable, soon coagulates; the precipitate is found to consist of a mixture of cadmium and its hydroxide. Copper also behaves

similarly, the sol is unstable and the precipitate is a mixture of metallic copper and carbon.

It may be prepared by placing a carbon electrode, on which the deposits of the above substances were made, be fitted with a platinum cup as shown in the figure and mercury placed in it, then on lighting an arc between the mercury and the carbon electrodes, a copious formation of the sol of mercury is observed. This sol has a grayish color and is not brown as observed by Lottermoser.¹

The sol is quite stable. On the addition of hydrochloric acid, there is a precipitate, which does not dissolve in excess of concentrated hydrochloric acid, even on long standing and vigorous shaking. The filtrate also does not give any test of mercury salts. Evidently, colloidal solution of mercury is obtained in a state of great purity. The sol is charged negatively, as shown by its migration in an electric field.

This method is very rapid and gives very good yield with mercury, and is also very convenient.

The works of Traube-Mengarini and Scala² and Masamichi Kimura³ show that heat alone may lead to the formation of sols. While trying to prepare a sol of α -naphthol or of mercuric iodide by the first method, it was observed that both substances have appreciable solubilities at the boiling temperature of water. Now if such a solution be rapidly cooled by immersing a test tube containing the liquid in a freezing mixture of ice and common salt, a suspension of small crystals resembling a sol is formed. The sol is not so fine as those obtained by chemical methods, but it resembles ordinary sols in its behavior towards electrolytes. Thus the thermal effect may be conceived to be due to the solubility of the substance at the high temperature of the experiment.

The conditions of these experiments being such that a rapid fall from a high to a low temperature takes place, we may have a release of supersaturation in the form of fine particles, resulting in a sol.

Though such an explanation may be applied to special cases, it cannot explain all cases in general, since it depends on the specific nature of the substance and the medium.

The process of sol formation by the electric method is that as already stated, under the intense heat of the arc discharge, the electrodes volatilize and subsequently, being condensed, form sols.

Many metals react very rapidly at this high temperature with water and although the substances are very rapidly cooled, yet there is time for their action on water to take place. This is shown by the fact that

¹ *J. prakt. Chem.*, [ii] **57**, 484 (1898).

² *Mem. R. Accad. Lincei*, [v] **8**, 576 (1911).

³ *Mem. Coll. Sci. Eng. Kyôto*, **5**, 211 (1913).

the unstable sol of copper or cadmium consists of a mixture of the metal and the hydroxide.

It has been found out that the sol, when shaken with benzene, is divided into two parts, the hydroxide goes to the benzene layer while the metal remains in the aqueous layer. Copper sol prepared by Bredig's method was observed to be a mixture of the metal and the hydroxide. Blake¹ has observed that silver sol by Bredig's method reacts alkaline. In this case the particles consist mainly of the free metal but the little silver oxide (Ag_2O) present is sufficient to produce a red coloration with phenolphthalein, since silver hydroxide (AgOH) is a strong base.

The stability of metal sols prepared by these methods in water can be easily understood if we view it in the light of the above remarks. We know that sols of Au, Pt, Ag, etc., are only stable in water when prepared by electric methods, whereas those of more electropositive metals are unstable. In the case of Au, Pt, Hg and Ag, there is very little or no chemical action between the metals and water, so that the sol obtained consists entirely of metallic particles as shown by analysis.

In the cases of Cu, Cd, etc., we have a mixture of metal and its hydroxide due to chemical action with water.

Now the colloidal metallic hydroxides show electric migration to the cathode and hence are positively charged, the opposite is the case with the metallic particles. As a consequence, a colloidal solution of the one precipitates that of the other. This seems to be the explanation of the varying stability of different metallic sols in water prepared by these methods.

It is seen that a silver sol prepared by Bredig's method is fairly stable, though it has been found to be alkaline to indicators. The very small amount of Ag_2O formed remains completely in the state of ordinary solution and not as a sol, since no trace of alkali or Ag_2O is obtained in the coagulum produced by neutral electrolytes. It is well known that alkalis in very small concentrations stabilize a metallic colloidal solution and hence the small amount of alkali due to the solution of silver hydroxide makes the silver sol more stable. Consequently, the foregoing explanation can be consistently applied in the study of the stability of metallic colloidal solutions in general prepared by electric methods in water.

In conclusion, it may be stated that the high temperature of the arcing electrodes may explain the formation of sols simply as a thermal process.

My best thanks are due to Professors Rây and Bhaduri.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA, INDIA.

¹ *Am. J. Sci.*, [iv] 16, 431 (1903).

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, COLLEGE OF THE CITY OF NEW YORK.]

THE DETECTION OF BROMIDES IN THE PRESENCE OF THIOCYANATES, CYANIDES AND FERROCYANIDES.

By LOUIS J. CURTMAN AND ALAN G. WIKOFF.

Received December 4, 1914.

It was found some two years ago in this laboratory that the presence of thiocyanates interfered with the test for bromides by the chlorine-water method. While this investigation was in progress, Guareschi¹ published a method for overcoming this interference. His procedure, however, requires special apparatus and does not provide the means of roughly estimating the quantities of bromides present. It was, therefore, thought worth while to continue our work, the object of which was to determine the extent of this interference and to devise a simple and rapid method for overcoming this difficulty in the detection of bromides. Finding that cyanides and ferrocyanides also interfere, this investigation was extended to include these acid radicals. Ferricyanides do not interfere, it being possible to detect easily one milligram of bromine as potassium bromide in the presence of 500 mg. of ferricyanide by means of chlorine water.

Determination of the Interference.---Chlorine water saturated at room temperature was employed throughout this work and was kept in small glass-stoppered bottles of amber-colored glass. In making the tests, precautions were taken to maintain its strength by not allowing the bottle to stand open for any considerable length of time. In determining the amount to be used, it was found that with 3 drops of chlorine water, an excellent test was obtained with 1 mg. of Br as KBr, which was not appreciably improved by the further addition of a drop or two. It was also found that three drops of chlorine water gave a good test with 20 mg. of Br as KBr, although in this case all the bromine was not liberated. For the extraction of the liberated bromine, carbon disulfide was chosen as the solvent.

The general procedure was as follows: From a buret a definite volume of a standard potassium bromide solution was run out into a test tube. To this were added successively one drop of 10% hydrochloric acid, a definite volume of a standard solution of the potassium salt of the interfering acid, 0.5 cc. of carbon disulfide, and sufficient distilled water to make the volume up to 5 cc. Three drops of saturated chlorine water were then introduced and the mixture shaken. The results are shown in the tables.

All these tests were repeated with the same results. It is evident from an examination of the tables that thiocyanates offer the greatest and ferrocyanides the least interference.

¹ *Atti. accad. sci. Torino*, 49, 15-21; *C. A.*, 8, 1938.

TABLE I.

Interference of Thiocyanates.

| 0.25 mg. CNS. | Test. | 0.20 mg. CNS. | Test. | 0.15 mg. CNS. | Test. |
|---------------|----------|---------------|--------------------|---------------|--------------------|
| 1 mg. Br | Negative | 10.0 mg. Br | Faint | 1.0 mg. Br | Good |
| 5 mg. Br | Negative | 1.0 mg. Br | Faint | 0.5 mg. Br | Fair |
| 20 mg. Br | Negative | 0.5 mg. Br | Very faint (limit) | 0.3 mg. Br | Faint |
| | | | | 0.1 mg. Br | Very faint (limit) |
| | | | | 0.05 mg. Br | Negative |

TABLE II.

Interference of Cyanides.

| 1 mg. CN. Test. | 0.8 mg. CN. Test. | 0.3 mg. CN. Test. | 0.1 mg. CN. Test. |
|-----------------|-------------------------------|---------------------|-------------------|
| 1 mg. Br Neg. | 1.0 mg. Br Faint | 1.0 mg. Br Good | 1.0 mg. Br Excel. |
| 5 mg. Br Neg. | 0.5 mg. Br Very faint (limit) | 0.5 mg. Br Fair | 0.5 mg. Br Good |
| 10 mg. Br Neg. | | 0.4 mg. Br Fair | 0.1 mg. Br Faint |
| 20 mg. Br Neg. | | 0.2 mg. Br Faint | 0.05 mg. Br Limit |
| | | 0.1 mg. Br Negative | |

TABLE III.

Interference of Ferrocyanides.

| 4.0 mg. $\text{Fe}(\text{CN})_2^{\text{IV}}$. Test. | 3.5 mg. $\text{Fe}(\text{CN})_2^{\text{IV}}$. Test. | 3 mg. $\text{Fe}(\text{CN})_2^{\text{IV}}$. Test. | 2.0 mg. $\text{Fe}(\text{CN})_2^{\text{IV}}$. Test. |
|--|--|--|--|
| 1 mg. Br Neg. | 1.0 mg. Br Faint | 1.0 mg. Br Fair | 1.0 mg. Br Fair |
| 5 mg. Br Neg. | 0.5 mg. Br Faint | 0.5 mg. Br Fair | 0.5 mg. Br Fair |
| 10 mg. Br Neg. | 0.4 mg. Br Very faint | 0.4 mg. Br Fair | 0.3 mg. Br Faint |
| 20 mg. Br Neg. | 0.3 mg. Br Negative | 0.3 mg. Br Faint | 0.1 mg. Br Very faint (limit) |
| | | 0.2 mg. Br Negative | |

The above results may be accounted for on the supposition that the chlorine water exercises a selective action, oxidizing the interfering substance first before liberating the bromine from the bromide. Thus in Table I we see that the 3 drops of chlorine water added were sufficient to oxidize 0.15 mg. of CNS and still leave sufficient chlorine to liberate the bromine as indicated; while when 0.20 mg. CNS were present there was only a very small amount of chlorine left after the CNS had been oxidized, and hence the tests were faint. With 0.25 mg. CNS all the chlorine was consumed, and hence it was impossible to detect the bromine, however great it might be. If this theory be true, it should be possible by the continued addition of chlorine water to provide an excess over that required to oxidize the interfering substance and thus obtain a positive test in those cases where negative results were obtained with a limited amount of chlorine. This conjecture is confirmed only to a limited extent by the experimental evidence; for it was found that there is a limit in this case beyond which no amount of chlorine water will produce a positive result.

A determination of the limits was made by ascertaining in what amounts of interfering substances 1 mg. of bromine could be detected by the repeated additions of chlorine water, adding the latter 3 drops at a time and shaking after each addition.

TABLE IV.
3-5 cc. Chlorine Water.

| 1 mg. Br. | | 1 mg. Br. | | 1 mg. Br. | |
|------------|----------|-----------|----------|---|-----------|
| 10 mg. CNS | Negative | 10 mg. CN | Negative | 40 mg. $\text{Fe}(\text{CN})_6^{\text{iv}}$ | Negative |
| 4 mg. CNS | Negative | 5 mg. CN | Negative | 30 mg. $\text{Fe}(\text{CN})_6^{\text{iv}}$ | Fair |
| 2 mg. CNS | Fair | 4 mg. CN | Faint | 20 mg. $\text{Fe}(\text{CN})_6^{\text{iv}}$ | Good |
| 1 mg. CNS | Good | 2 mg. CN | Fair | 10 mg. $\text{Fe}(\text{CN})_6^{\text{iv}}$ | Very good |
| | | 1 mg. CN | Good | | |

After much experimentation the following procedure was devised for the detection of bromides in the presence of thiocyanates, cyanides and ferrocyanides, based upon the precipitation of the respective radicals as cuprous salts in presence of sulfurous acid.

Method.—The solution to be tested, which should be neutral or slightly acid with sulfuric acid, is treated with 15 cc. of a saturated solution of SO_2 (this amount has been found by experiment to be sufficient to insure the precipitation of 500 mg. of CNS, CN or $\text{Fe}(\text{CN})_6^{\text{iv}}$ as their cuprous salts). The solution is now heated just to boiling, and while hot it is treated with constant stirring with 2 *N* CuSO_4 solution, which should be slowly run out from a buret or dropping funnel. Enough CuSO_4 must be added to insure an excess, shown by the blue color of the supernatant liquid. (In the presence of CNS a green liquid indicates insufficient H_2SO_3 and more must be added until the solution becomes blue. This is important since the green solution still contains CNS which has not combined with the copper and which, therefore, will interfere with the subsequent test for bromine.) Filter while hot, wash twice with distilled water, adding the washings to the main filtrate contained in an Erlenmeyer flask. Boil down the filtrate to about 5-10 cc. (This removes the excess of SO_2 and reduces the volume so that the final test may be made in a test tube. A slight white precipitate may form during this operation but may be disregarded.) Cool the contents of the flask¹ and pour into a test tube. Rinse the flask with 3-4 cc. distilled water and add to the liquid in the test tube. Add 1 cc. of 3 *N* H_2SO_4 , 1 cc. 1% KMnO_4 , and shake.² Now add not more than 0.5 cc. CS_2 and shake. A yellow color in the CS_2 layer proves the presence of Br.

The acid and KMnO_4 are added and shaken first in order that the CS_2 may not be in contact with the KMnO_4 any longer than is necessary, since they react with the formation of a small amount of MnO_2 which with vigorous shaking may dissolve in the CS_2 , yielding a color indistinguishable from that given by small amounts of Br. An excess of CuSO_4 is not ob-

¹ This may be easily accomplished by holding the flask under the tap of running cold water.

² Dilute HCl and Cl water may be used instead of the H_2SO_4 and KMnO_4 ; but the former has the disadvantage that the solution cannot subsequently be tested for chlorides.

jectionable since CuSO_4 in the presence of KMnO_4 liberates all the Br from KBr .¹

The following tests show the reliability of the method:

TABLE V.

| No. | Mg. Br. | Mg. CNS. | Mg. CN. | Mg. $\text{Fe}(\text{CN})_2$ ^{iv} . | Results. |
|-------|----------|----------|---------|--|---------------------|
| 1 | 0.0 | 250 | ... | ... | Absolutely no color |
| 2-5 | 1.0 | 250 | ... | ... | Negative |
| 6-7 | 1.5 | 250 | ... | ... | Fair |
| 8-16 | 2.0-3.0 | 250 | ... | ... | Good |
| 17-20 | 4.0-10.0 | 250 | ... | ... | Strong color |
| 21-25 | 2.0 | 500 | ... | ... | Good |
| 26 | 4.0 | 500 | ... | ... | Excellent |
| 27 | 1.0 | ... | 500 | ... | Negative |
| 28-30 | 2.0 | ... | 500 | ... | Excellent |
| 31 | 1.0 | ... | ... | 500 | Negative |
| 32-34 | 2.0 | ... | ... | 500 | Excellent |
| 35 | 2.0 | 200 | 150 | 150 | Good |
| 36 | 2.0 | 300 | 100 | 100 | Good |
| 37 | 2.0 | 100 | 200 | 200 | Good |
| 38 | 2.0 | 400 | 50 | 50 | Good |

The average time required for the completion of a test was 15 min.

Summary.

1. Attention has been called to the interference of thiocyanates, cyanides and ferrocyanides in the detection of bromides by the ordinary methods.
2. The interference offered by each of these substances has been determined.
3. A rapid method has been devised which is capable of detecting 2 mg. of bromine in the presence of 500 mg. of each of the interfering substances.
4. Numerous test experiments show the method to be trustworthy.

NEW YORK, N. Y.

ON FRACTIONAL DISTILLATION WITH REGULATED STILLHEADS.

[FIRST COMMUNICATION.]

CASES IN WHICH THE BOILING-POINT CURVE PASSES THROUGH A MAXIMUM OR A MINIMUM.

BY M. A. ROSANOFF AND C. W. BACON.

Received December 31, 1914.

Section 1. Introductory.

A recent joint communication² outlined a theory of fractional distillation based on a new relationship between the slopes of the total pressure curve and the relative compositions of the liquid mixtures and the corresponding vapors. In the mathematical treatment it was assumed that

¹ Prescott and Johnson's "Qualitative Analysis," p. 346.

² Rosanoff, Bacon, and Schulze, *THIS JOURNAL*, 36, 1993 (1914).

the process involved no reflux condensation whatever, that is, that the vapors escaped without any part of them undergoing liquefaction on the way and returning to the still. This is the simplest thinkable type of distillation, and, therefore, of unquestionable interest theoretically. As an actual means of separating the constituents of liquid mixtures, whether for scientific or industrial purposes, it is not used. For hundreds of years¹ chemists have purposely employed partial reflux condensation to produce as wide a difference between the distillate and the residue in the still as can be conveniently brought about in a single operation, and thus increase the efficiency of fractional distillation.

F. D. Brown² differentiates two processes by which partial reflux condensation is brought about in the various forms of apparatus in general use. To quote from Brown's own statement: "Though differing much in detail, they [the various apparatus] are all designed to subject the mixed vapors to one or both of two well-defined processes, which may be termed respectively *washing* and *cooling*. In the process of *washing*, the mixed vapors issuing from the still are made to pass through several layers of liquid obtained by their own partial condensation, they are thus *washed* by these successive layers, and it is supposed that the vapor of the liquid of highest boiling point is partially removed by this process, which results, therefore, in a distillate containing more of the liquid of lower boiling point than would be obtained by simple distillation In the process of *cooling*, the mixed vapors are partially condensed, either by allowing radiation to take place, or by passing them through a coil kept at a given temperature; the liquid of highest boiling point suffers, of course, the most condensation, and runs back into the still, a better distillate being thus obtained With a view to learning whether these two processes of *washing* and *cooling* really differ in their effects, I have made the experiments now to be described."

In the present state of knowledge no experiments would be necessary to prove that partial condensation by washing and partial condensation by cooling are different processes. Thus numberless cases might be specified in which a colder mixed vapor would be partially condensed by passing through a *hotter* mixed liquid. In such cases "cooling" is out of the question, yet partial condensation would take place, due to what Brown calls the "washing" of the vapor. Brown demonstrated the difference between washing and cooling by fractionating mixtures of carbon disulfide and benzene under suitably varied experimental conditions. The results are summed up by his statement (p. 56): "These distillations prove conclusively that the processes of *washing* and of *cooling* are not identical."

¹ See Young, "Fractional Distillation" (London, 1903), p. 154.

² Brown, *Trans. Chem. Soc.*, 37, 49, 50 and 56 (1880).

In the stillheads or columns generally used, the processes of washing and cooling are more or less intimately combined, for the ascending vapor is not only washed, but also cooled, by the reflux condensate. Nevertheless, it is certain that the main process by which the efficiency of such apparatus is determined, is washing; and a vast majority of the patented improvements consist in the introduction of ingenious "traps" in which the vapors are thoroughly washed in pools of the reflux condensate. Where cooling devices proper are employed at all, they play a decidedly subordinate role.

That distillation depending principally, almost exclusively on *cooling*, may have important possibilities of its own, has long been suspected, and attempts have been made to rationalize fractional distillation by the use of a non-washing stillhead kept at a constant temperature. The first to employ such a stillhead practically (in the fractionation of petroleum, coal tar, and other mixtures) was C. M. Warren, of Boston, who believed that the method promised results of great value.¹ The first to investigate the working of a regulated stillhead systematically was F. D. Brown,² who improved Warren's stillhead and made extensive observations on the effect of cooling a saturated binary vapor to a given constant temperature. Brown sums up his results in the following important statement: "*In distillation with a stillhead maintained at a constant temperature the composition of the distillate is constant, and is identical with that of the vapour evolved by a mixture whose boiling point equals the temperature of the stillhead.*"

An attempt to utilize the regulated stillhead was also made by Lord Rayleigh.³ On the other hand, Carveth⁴ experimented with a combination of the washing and the cooling processes by filling a tin pipe condenser with intercepts and maintaining the pipe at a constant temperature.⁵ Finally, Sydney Young and Thomas⁶ obtained valuable results by connecting in series a dephlegmator (washing column) and a regulated temperature stillhead, as is frequently done in the industries. But these studies have thrown no new light upon the regulated stillhead theoretically.

In course of the past five years, the working of the regulated stillhead has been fully reinvestigated by one of us with several collaborators. It was found that Brown's law requires serious modification, and that only in its true form can it serve as the basis of a rational, almost ideal, process of fractional distillation, such as the previous investigators have searched for in vain. The modified law, and the process of distillation based upon

¹ Warren, "Memoirs of the American Academy," New Series, 9, 121 (1864), and *Ann.*, 4 (Supplementband), 51 (1865).

² Brown, *J. Chem. Soc.*, 37, 49 (1880), and especially *Ibid.*, 39, 517 (1881).

³ Lord Rayleigh, *Phil. Mag.*, [VI] 4, 535 (1902).

⁴ Carveth, *J. Phys. Chem.*, 6, 253 (1902).

⁵ An arrangement similar in principle had already been employed by Perrier.

⁶ Young and Thomas, *J. Chem. Soc.*, 71, 440 (1897).

it, will be discussed in a series of communications to which the present paper may serve as an introduction.

The main object of this present communication is to point out how the regulated stillhead should be expected to function in those numerous cases in which the boiling-point curve passes through a maximum or a minimum; in which, therefore, there may be *two* mixtures boiling at one and the same temperature: in the words of Brown's law, *two mixtures* "whose boiling point equals the temperature of the stillhead."

Section II. Brown's Law in the Cases under Consideration.

Let us assume for the present that Brown's law is true in its original form, as expressed above. And considering a simple case, like that of carbon disulfide and carbon tetrachloride, where the boiling points of all mixtures are intermediate between those of the isolated components, let the temperature of a regulated stillhead be made equal to the boiling point of the more volatile component. Then, by the original Brown law, no matter what the composition of the mixture boiling in the still, the escaping vapor should consist almost entirely of that component.

On the other hand, suppose we are dealing with a pair of substances whose boiling-point curve passes through a minimum. And, while any given mixture of the two is boiling in the still, let the stillhead, originally cold, be heated to the boiling temperature of the most volatile mixture (*i. e.*, the one having the minimum boiling point). The vapor from such a mixture has the same composition as the mixture itself, and, therefore, if Brown's law is correct, that should also be the composition of the escaping vapor, no matter what mixture is at any given instant boiling in the still. But next let us still further raise the temperature of the stillhead, and fix it at the boiling point of the more volatile component. Now the stillhead temperature is really equal to the boiling point of two different liquids: the more volatile component pure and a certain mixture. The vapors given off by the two liquids are, of course, different: in one case a single substance, in the other a mixture. Which of the two vapors will be escaping from the stillhead?

Brown's experiments with the pairs carbon disulfide-alcohol and carbon disulfide-ethyl acetate taught him that it is the *mixed* vapor that is produced invariably.¹ In the case of carbon disulfide and alcohol, keeping the stillhead at the boiling point of pure carbon disulfide, Brown obtained a uniform distillate containing about 87.3% of carbon disulfide. In the case of carbon disulfide and ethyl acetate, with the stillhead at the boiling point of pure carbon disulfide, he obtained a uniform distillate containing about 72.6% of carbon disulfide.

Brown says nothing as to the effect of keeping the stillhead at temperatures *intermediate* between the boiling point of the most volatile mixture

¹ Brown, *J. Chem. Soc.*, 39, 529 (1881).

and that of the isolated more volatile component—temperatures at which two different mixed vapors should be expected according to his law. Nor does he refer at all to those cases in which the boiling-point curve passes through a maximum, and in which, therefore, two different mixed vapors might be expected at any stillhead temperature intermediate between the boiling point of the least volatile mixture and that of the isolated less volatile component. He evidently felt that an experimental elucidation of the subject would be of value; for he expresses the hope of returning to the problem in a future communication. This he never did. Nor is the subject at all mentioned in the more recent monograph literature on heterogeneous equilibria or fractional distillation.

At the present time, especially if we employ the form of diagram (see Fig. 1) in which both the boiling-point curve and the dew curve (vapor-composition curve) are plotted with respect to abscissae representing the composition of liquid mixtures, the question as to which of the two possible

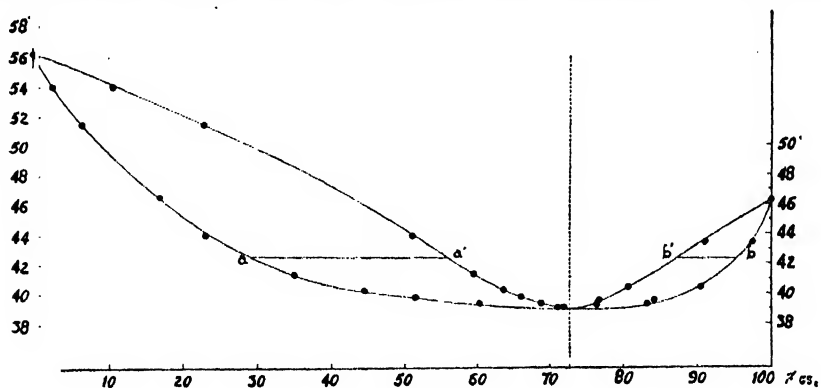


Fig. 1.

mixed vapors should be expected in accordance with Brown's law, presents no real difficulty. Since distillation with a regulated stillhead cannot affect the composition of a mixture of maximum or minimum boiling point, it is almost obvious that in all cases of the type in question the diagram should be divided into two parts by a straight line perpendicular to the composition-axis and passing through the maximum, or the minimum, of the boiling-point curve, and each part should be considered as an independent diagram by itself. The composition of the resulting vapor would then appear to depend upon whether the composition of the liquid in the still is comprised in the right-hand or the left-hand part of the diagram. For example, in our Fig. 1, which pictures the case of carbon disulfide and acetone, let the stillhead temperature be at the height of the lines aa' , $b'b'$. Then it is obvious in the first place that the stillhead will have no effect at all if the liquid in the still corresponds to any point

lying between a and b ; for any such liquid would boil below the temperature of the stillhead, and a hot stillhead cannot condense a cold vapor. But further we should expect that if the composition of the liquid boiling in the still is represented by a point lying to the left of a , the stillhead will deliver a uniform vapor of the composition a' ; if the liquid boiling in the still has a composition lying to the right of b , then the stillhead, *at the same temperature as before*, will yield a uniform vapor of the composition b' .

Trustworthy as these theoretical expectations appear, it nevertheless seemed desirable to carry out a series of experiments, to obtain a practical demonstration of their correctness. The results are reproduced below.

Section III. The Apparatus.

Our apparatus (Fig. 2) was similar in principle to the one employed, in a former study, by Rosanoff, Lamb, and Breithut.¹ It consisted of a large double-walled cylinder of tinned copper, without top or bottom, fastened within a cylindrical tank full of water. The closed annular space between the walls of the copper cylinder was connected with the still below by a brass pipe passing through the bottom of the outside tank, near the rim. A similar pipe, serving as a delivery tube, and passing through the side of the outside tank, near the top, connected the annular space with a condenser. The lower edge of the double-walled cylinder was in a plane slanting downward toward the still, to permit any condensate within the annular space to flow back without forming a pool at the bottom. The water in which the double-walled cylinder was immersed was kept in vigorous motion by a pair of horizontally revolving fans whose diameter was little less than the internal diameter of the copper cylinder, and which acted with the effect of an Archimedes screw. In this manner uniform temperature was secured throughout the tank, an electric regulator maintaining the temperature of the bath constant within $\pm 0.02^\circ$. The greatest height of the double-walled cylinder was 76 cm.; its smallest height was 70 cm.; the mean diameter was 25 cm.; and the annular space between the walls was 0.95 cm. wide. It may be positively stated that a stillhead of this form is greatly superior to the coil condensers used by previous investigators.

The substances used were purified, and our consecutive distillates were analyzed, in the manner described in a former communication.²

And first of all, the efficiency of our regulated stillhead was subjected to test in the case of carbon disulfide-carbon tetrachloride, which is not complicated by either a maximum or a minimum in the boiling-point curve. A mixture containing slightly over 26% of carbon disulfide was introduced

¹ Rosanoff, Lamb, and Breithut, *THIS JOURNAL*, 31, 454 (1909); *Z. physik. Chem.*, 66, 356 (1909).

² Rosanoff, Bacon and White, *THIS JOURNAL*, 36, 1803 (1914).

into the still, and the temperature of the stillhead was maintained constant at $59.82^{\circ} \pm 0.02^{\circ}$. Theoretically, *i. e.*, according to Brown's law, the

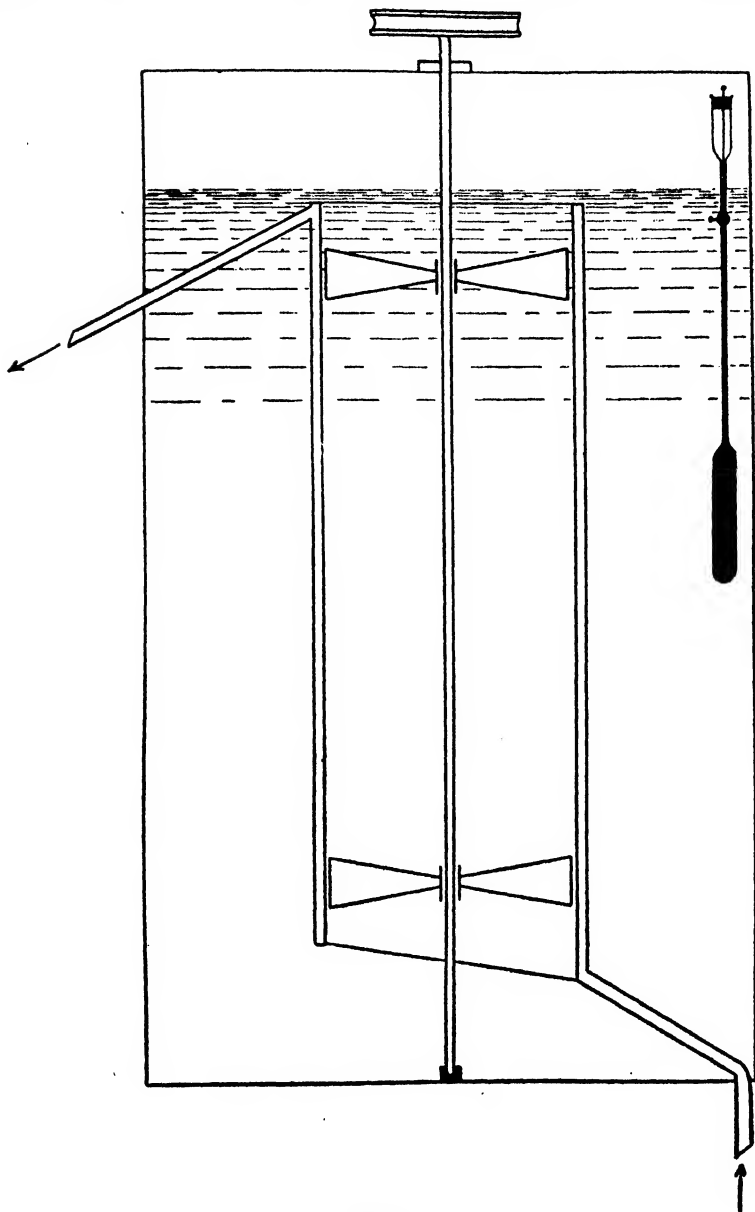


Fig. 2.

distillates were expected to contain 60.8% CS_2 . Seven consecutive fractions were actually found to contain 60.8, 60.7, 60.7, 60.5, 60.7, 60.5,

60.7, 60.7, and 60.7% of carbon disulfide, respectively. The reliability of the apparatus was thus demonstrated.

Section IV. Results.

Case 1. Carbon Disulfide and Acetone.—In this case the boiling-point curve passes through a *minimum*.¹

In a first experiment a mixture containing only a small percentage of acetone was introduced into the still. The temperature of the stillhead was kept constant at $40.02^{\circ} \pm 0.01^{\circ}$. Seven consecutive fractions of the distillate contained: 75.2, 75.2, 75.1, 75.1, 75.1, 75.1, and 75.1 molar per cent. of carbon disulfide, respectively.

In a second experiment, we introduced into the still a mixture containing only 29% CS_2 (a composition lying within the left-hand part of the diagram). The temperature of the stillhead was again kept at $40.02^{\circ} \pm 0.01^{\circ}$. Yet this time fifteen consecutive fractions of the distillate were found to contain, respectively, 55.4, 55.3, 55.4, 55.4, 55.4, 55.3, 55.4, 55.4, 55.4, 55.4, 55.2, 55.4, 55.3, and 55.3 molar per cent. of carbon disulfide.

Case 2. Ethyl Iodide and Ethyl Acetate.—In this case again the boiling point passes through a *minimum*.

In a first experiment a mixture containing only a small percentage of ethyl acetate was introduced into the still, and the temperature of the stillhead was fixed at $71.22^{\circ} \pm 0.02^{\circ}$. Four consecutive fractions of the distillate contained 89.9, 89.3, 89.2, and 89.1 molar per cent. of ethyl iodide, respectively.

In a second experiment a mixture of roughly equal parts of the two components was introduced into the still. The temperature of the stillhead was the same as in the first experiment. But this time four consecutive fractions of the distillate were found to contain, respectively, 49.4, 49.3, 48.9, and 48.9 molar per cent. of ethyl iodide. In this case the uniformity of the distillates was not as perfect as before. Nevertheless the two experiments illustrate the question involved sufficiently well.

Case 3. Chloroform and Acetone.—In this case the boiling-point curve passes through a *maximum*.

Two experiments again were performed. In the first, a mixture containing roughly 6% of acetone (a composition lying to the right of the maximum) was introduced into the still. The temperature of the stillhead was fixed at $62.02^{\circ} \pm 0.01^{\circ}$. Six consecutive fractions of the distillate were found to contain, respectively, 92.4, 92.4, 92.4, 92.5, 92.3, and 92.3 molar per cent. of chloroform.

In the second experiment the mixture originally introduced into the still contained something over 40% CHCl_3 (a composition lying to the left of the maximum). The temperature of the stillhead was again maintained

¹ This case is illustrated by Fig. 1, in which, however, the abscissae represent *weight per cents*.

at 62°. This time, however, six fractions of the distillate were found to contain, respectively, 30.8, 30.8, 30.9, 30.8, 30.9, and 30.9 molar per cent. of chloroform.

As already stated, changes in Brown's law itself will be proposed in communications to follow. Here we would again express our thanks to the Rumford Committee of the American Academy for a grant in aid of our researches.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH,
UNIVERSITY OF PITTSBURGH.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. NO. 19.]

THE MEASUREMENT OF VAPOR PRESSURE LOWERING BY THE AIR SATURATION METHOD.¹

BY EDWARD W. WASHBURN AND EDWARD O. HEUSE.

Received December 16, 1914.

1. Introduction.

The importance of having a reasonably accurate method for investigating the molecular character of aqueous solutions over a considerable concentration range and at a constant temperature led to an attempt to improve the vapor pressure method so that it might be employed for this purpose. The experimental work in connection with the problem was begun in 1909 by Mr. H. B. Gordon. He was able to show that the method could be made to give the desired accuracy and in addition to building and testing the apparatus he also measured the vapor pressure lowering of several aqueous solutions. The results of his work together with a comparative discussion of previous investigations in the same field were printed and distributed in 1912 in the form of a Doctor's Thesis,² but were not formally published. In September 1912 the experimental work was taken up by Mr. E. O. Heuse and is being carried on by him at the present time. A description of the theory of the method together with some of the results obtained was presented at the Chicago meeting of the American Physical Society, November, 1914, and published in abstract in the *Physical Review*.

The appearance of a recent paper by Frazer and Lovelace³ on an improved *static* apparatus for measuring vapor pressure lowering seems to make it worth while to publish a description of our apparatus and method at this time, for purposes of comparison, postponing until later

¹ This paper is an abstract of a thesis presented to the Graduate Faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1914.

² H. B. Gordon, Univ. of Ill. Theses, 1912.

³ Frazer and Lovelace, *THIS JOURNAL*, 26, 2439 (1914).

the presentation and theoretical interpretation of the vapor pressure data which have been collected with it.

2. Outline of the Method.

The dynamic or air-saturation method when employed for the purpose of measuring the difference between the vapor pressure (p_0) of a solvent and that (p) of a solution has usually been carried out by determining each of these quantities separately and then subtracting one from the other. This procedure gives a very low degree of accuracy on the vapor pressure lowering, the chief sources of error being (1) in the measurement of the quantity of air aspirated and (2) in maintaining the average temperature of two successive experiments sufficiently constant. The obvious modification which is necessary in order to eliminate these two sources of error is to pass the same air (whose quantity, therefore, need not be known) over the solution and the solvent in succession, each liquid being contained in a suitable "saturator" and both saturators being placed beside each other in a well stirred thermostat. Then one may either determine the losses in weight of the two saturators by weighing them before and after the experiment, as in the method of Ostwald-Walker or one may absorb the moisture in absorbers of such form and size that they can be accurately weighed. The former method has been successfully carried out by Berkeley, Hartley and Burton¹ with aqueous solutions at 0°. The latter method seemed preferable to us, however, because it involved no change in the concentration of the solution during the run and the volume of air and its rate of flow could be made as large as desired, since there was no necessity of employing a small and compact saturator as is the case when the saturator has to be weighed.

Our apparatus, therefore, has been constructed so as to embody the advantages of the differential procedure first used by Ostwald and Walker with those of the absorption method which has been employed by most investigators in this field. The type of absorber which we have employed coupled with the comparatively high rate of aspiration used necessitates the use of small differential manometers for the purpose of measuring the fall in pressure through the apparatus. With a different type of absorber cooled with liquid air, these manometers could probably be dispensed with.

3. Calculation of the Relative Vapor Pressure Lowering.

The following method of computing the results of an experiment conducted as outlined above is applicable to moderate temperatures: At high temperatures, where the deviation of saturated water vapor from Boyle's law is large, corresponding modifications must be made in the method of calculation, but these will not be entered into here.

¹ Berkeley, Hartley and Burton, *Phil. Trans.*, (A) 209, 177 (1909).

The mass, m , of water necessary to saturate a volume, v , of air in order to bring it into equilibrium with a liquid whose aqueous vapor pressure is p is expressed by the equation

$$m = Kpv \quad (1)$$

where K is a proportionality constant. In the method just outlined the same air is passed through both saturators and hence the volume emerging from a saturator will vary inversely as the partial pressure of the air in that saturator. Obviously, this is in each case the atmospheric pressure diminished by the vapor pressure of the liquid with which the air is in equilibrium and by the difference between the total pressure within the saturator and the atmospheric pressure. It therefore follows that

$$\frac{v_1}{v_2} = \frac{B - p_2 - \Delta P_2}{B - p_1 - \Delta P_1} \quad (2)$$

where the subscripts indicate whether the quantity is measured at the outlet of the first or the second saturator of the train. B is the barometric pressure and ΔP the difference between this pressure and that within the saturator as measured by a differential manometer.

From (1) it follows that the ratio of the masses of water absorbed by the two absorbers will be

$$\frac{m_1}{m_2} = \frac{p_1 v_1}{p_2 v_2} \quad (3)$$

If the second saturator contains pure water ($p_2 = p_o$) and the first saturator an aqueous solution ($p_1 = p$), we have from (2) and (3)

$$p = \frac{mp_o(B - \Delta P_1)}{m_o(B - p_o - \Delta P_2) + mp_o} \quad (4)$$

Dividing both sides of Equation 4 by p_o , subtracting each side from unity, expressing the result in the fractional form and collecting terms, we have

$$r = \frac{p_o - p}{p_o} = \frac{(m - m_o)p_o + m_o(B - \Delta P_2) - m(B - \Delta P_1)}{(m - m_o)p_o + m_o(B - \Delta P_2)} \quad (5)$$

Putting $m_o - m = D_m$ and $\Delta P_2 - \Delta P_1 = D_p$ gives

$$r = \frac{p_o - p}{p_o} = \frac{D_m(B - \Delta P_1 - p_o) - m_o D_p}{m_o(B - \Delta P_2) - D_m p_o} \quad (6)$$

This is the expression for $\frac{p_o - p}{p_o}$ in terms of the quantities which are directly measured in the experiment. In order to make clear the relative importance of the different terms in this expression and their influences upon the accuracy of the result, we will substitute typical values for them as obtained in an actual experiment in which the solution employed was a molal solution of cane sugar. This gives

$$r = \frac{p_0 - p}{p_0} = \frac{0.2401(749.01 - 0.24 - 23.71) - 11.7458 \times 0.050}{11.7458(749.01 - 0.29) - 0.2401 \times 23.71} = \frac{174.1 - 0.59}{8794.2 - 5.6} = \frac{173.5}{878.9} = 0.0197. \quad (7).$$

Suppose for example that we desire an accuracy of 1% in value of r . Of the terms appearing in the denominator the last one, $D_m p_0$, is practically negligible in comparison with the first and in the first term the quantity ΔP_2 is practically negligible in comparison with B . At most an accuracy of a few tenths of a mm. in measuring ΔP_2 would be ample, and an accuracy ten times as great as this is easily attained. The degree of accuracy with which the denominator of Equation 6 is known depends, therefore, practically upon the accuracy with which m_0 and B can be measured, and it is clear that both of these quantities can be easily measured with 10 or 100 times the necessary accuracy. As far as the terms in the denominator are concerned we may, therefore, conclude that the errors involved in their measurement will not have any appreciable influence upon the accuracy of the result.

Turning to the numerator we note that the second term, $m_0 D_p$, is very small in comparison with the first, and that at most an accuracy of 0.05 mm. in the measurement of D_p would be ample. This degree of accuracy, and more, can be easily attained. In the first term of the numerator ΔP_1 is practically negligible while p_0 , the vapor pressure of the pure solvent at the temperature of the experiment, needs to be known with an accuracy of 7 mm. (*i. e.*, 30%) if it is not to influence the accuracy of the result by more than 1%. In the case of water it is of course known with an accuracy 100 times greater than this and in any case its determination with the necessary degree of accuracy offers no difficulties. We may conclude, therefore, that the percentage accuracy of the result is almost entirely determined by the percentage accuracy attainable in the quantity D_m , that is, the difference in the increases in mass of the two absorbers and this difference is itself directly determined by placing the absorbers on the opposite pans of a sensitive balance and adding the necessary weights to produce equality. This difference can be determined to 0.1 or 0.2 mg. and in the example taken this would amount to less than 0.1%. Practically, however, the accuracy of the final result is not determined by the accuracy in measuring the actual difference D_m obtained but rather in insuring such perfect experimental conditions that the observed D_m shall correspond to the actual pressure difference within the required limits. As will be seen later the degree of concordance in duplicate experiments is more nearly 0.5% in the case of a molal solution.

From this discussion of the theory of the differential method the following facts are brought out, which distinguish it from most of the previous

attempts to determine the vapor pressure lowering of aqueous solutions by means of the dynamic or air-saturation method:

(1) It is not necessary to measure or to know even approximately how much air is passed through the system during the experiment, and its amount may, therefore, be made as large as desired.

(2) In order to measure the relative lowering of the vapor pressure the individual vapor pressures themselves are not required, except a very rough value of p_0 , the vapor pressure of the pure solvent, an accuracy of a few mm. in the value of p_0 being amply sufficient.

(3) Temperature variations¹ as great as 1° during the course of an experiment would not appreciably influence the result for solutions of moderate concentrations provided the thermostat is kept thoroughly stirred.

4. Description of the Apparatus.

General Arrangement.—In the apparatus now in use *three* saturators are employed in each experiment, the first and third containing pure water and the second the solution under investigation. The general plan of the apparatus is shown diagrammatically in Fig. 1.

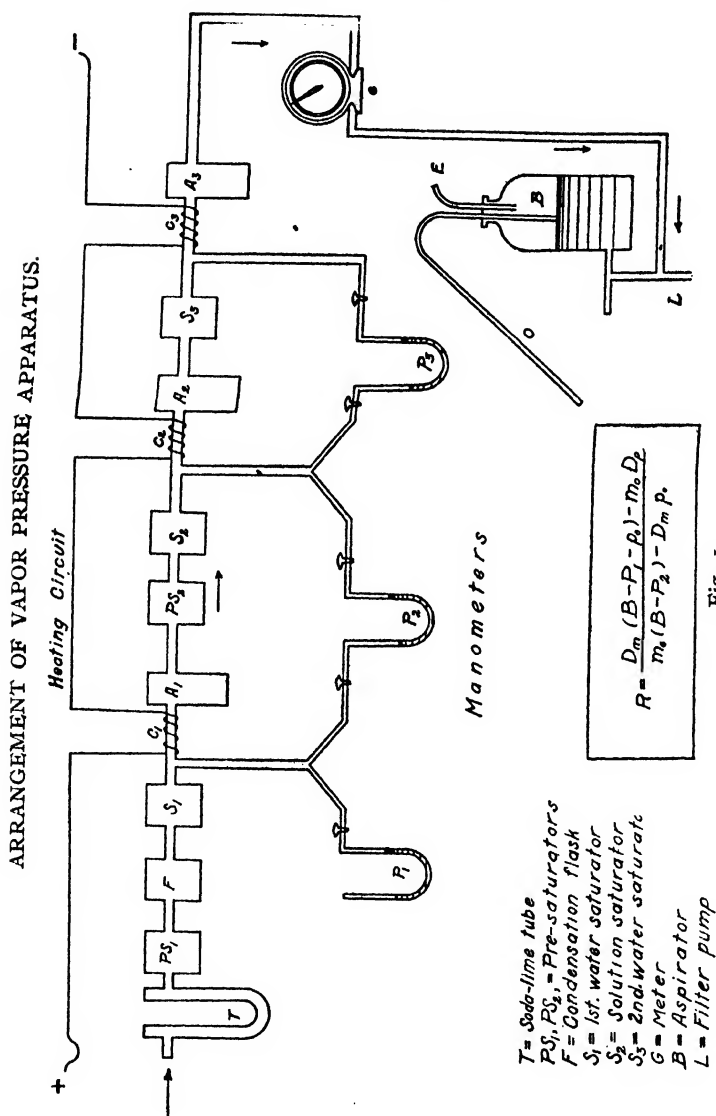
Air, drawn by the constant level aspirator *B* passes first through the soda lime tube, *T*, and then into the presaturator, *PS*₁, where it is *saturated* with water vapor at about 50° . The air then passes down into the flask *F* which is immersed in the thermostat and here it deposits most of its excess of moisture and enters the first saturator *S*₁ of the train slightly supersaturated. On emerging from this saturator it is in equilibrium with water at 25° . It then passes out of the thermostat through the tube *C*₁, which is surrounded by a heating coil and is heated to a temperature of about 30° before it emerges from the thermostat. The warm air then passes at once through the absorber *A*₁ where all of the moisture is removed. The perfectly dry air then goes through a second presaturator, *PS*₂, containing water at 25° where it takes up the bulk of the moisture necessary to bring it into equilibrium with the solution in saturator *S*₂. After passing through this saturator and its absorber, *A*₂, the perfectly dry air then passes directly into the third saturator, *S*₃, which contains pure water. In the first and third saturators equilibrium is always approached from *opposite directions* and a valuable check upon experimental conditions is thus obtained.

¹ The temperature coefficient of $r = \frac{p_0 - p}{p_0}$ is $\frac{100 \, dr/dt}{r} = 100 (1 + 1/r)$

$\frac{L_D}{RT^2}$ per degree where L_D is the differential heat of dilution (heat absorbed) per

mole of solvent. At 25° this becomes $\frac{100 \, dr/dt}{r} = 5.66 \cdot 10^{-4} (1 + 1/r) L_D$. Thus for a molal cane sugar solution L_D is about 2 cal. and $r = 0.02$. Hence the temperature coefficient of r for this solution is only 0.06% per degree.

The small differential manometers, M_1 , M_2 , M_3 connected (through stopcocks not shown) serve to measure the pressure differences ΔP_1 , ΔP_2 and ΔP_3 , respectively, under the



water of the thermostat are sealed glass joints, the whole apparatus being supported on a frame as shown in Fig. 2. The details of construction of the different parts follow.

The Saturators.—These are of the type devised by Berkeley and Hartley,¹ modified by the addition of the small bulbs at the ends as shown in Fig. 3 and Fig. 2. The horizontal tubes are filled about half full of

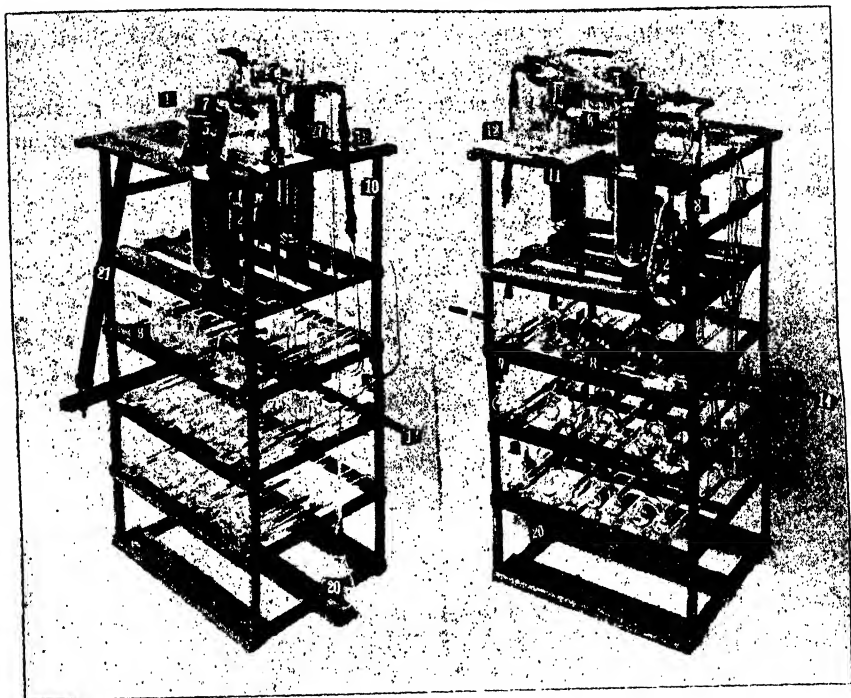


Fig. 2.

(Letters in parentheses refer to Fig. 1.) (1) Tubes leading to manometers. (2) Presaturator (PS_2) for solution. (3) Tube and heating coil (C_2). (6) P_2O_5 safety tube. (8) Saturator (S_2). (9) Point where the air enters the system. (13) Absorber (A_1). (14) Axle on which frame rocks. (20) Condensation flask (F).

liquid and then, as the platform on which the saturators are placed rocks slowly back and forth, the liquid flows from one end of the horizontal tubes to the other. The air which enters at the center of each horizontal tube passes around through

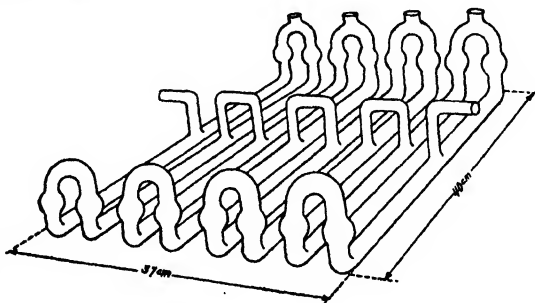


Fig. 3.

¹ Berkeley and Hartley, *Proc. Roy. Soc., (A)* 77, 156 (1906).

first one vertical connecting tube and then the other as the saturator tips back and forth. The air never bubbles through the liquid at any point. The small bulbs in the vertical connecting tubes are for the purpose of breaking liquid films which sometimes form in the case of certain solutions. The saturator for the solution contains quartz beads which roll back and forth and aid in keeping the solution stirred.

The Absorbers.—The type of absorber used for removing and weighing the water is shown diagrammatically in Fig. 4. Most of the water is condensed in the flask, *F*, which is cooled by an ice bath in a silvered Dewar tube. The air then passes over concentrated sulfuric acid contained in the four tubes, *A*.

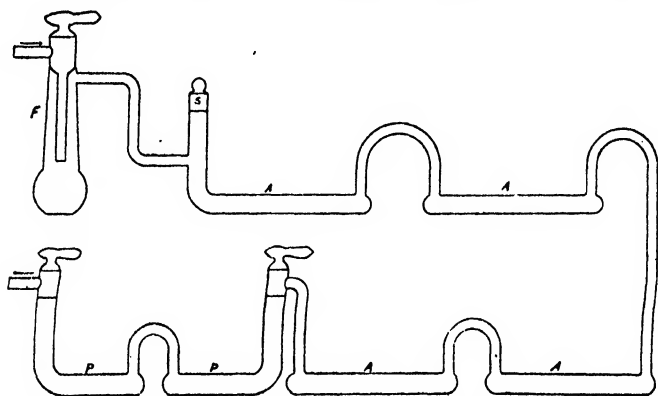


Fig. 4.

These tubes have a series of depressions or pockets (not shown in the figure) along the bottom for increasing the amount of sulfuric acid which they will contain. The two tubes, *P*, are about two-thirds filled with glass beads and phosphorus pentoxide and a removable pentoxide safety tube (not shown) completes the absorber and serves to prevent the diffusion of any moisture backward against the air current. The absorber is compactly built so that it will fit the pan of a sensitive balance. It is shown in position on the upper shelf of the support, at 13 in Fig. 2. About 25 g. of water can be condensed and absorbed in one absorber. The different absorbers are as nearly identical as possible in construction and when charged ready for use weigh about 300 g. each.

The Differential Manometers.—The small differential manometers, M_1 , M_2 , M_3 , shown in Fig. 1 are water manometers inclined at such an angle that 1 mm. of mercury is equivalent to 200 mm. of water. The angle of inclination was determined accurately by means of a cathetometer. The stopcocks which separate these manometers from the train are opened at intervals during the run and the readings of the manometers recorded.

When the experiment is proceeding properly these readings are practically constant throughout the run.

The Thermostat.—The apparatus and support as shown in Fig. 2 are immersed in a large water bath at such a depth that the three lower platforms and their saturators are completely covered. The whole support is then rocked back and forth on the axle (14, in Fig. 2) at the rate of four complete oscillations per minute. In addition to the stirring produced by this motion two powerful turbine stirrers and one propeller blade stirrer insure a uniform temperature throughout all parts of the thermostat. Three heaters symmetrically distributed and controlled by a hydrogen regulator served to keep the temperature constant.

With this arrangement the apparatus can be kept in continuous operation and as many runs as desired made with a given solution, the air current being interrupted only long enough to replace one set of absorbers by another. When a new solution is to be employed the apparatus is lifted out of the thermostat, the old solution removed with a pipet and the new one introduced. It is not necessary to take the apparatus apart for this operation. Previous to the first insertion of a weighed pair of absorbers in the train the air current is allowed to pass through the system for half an hour to insure equilibrium and proper working conditions. The barometer is read from time to time during the run. In one or two cases the occurrence of thunder storms during the run necessitated the use of a barograph record in finding the weighted time average of the barometric pressure during the run.

5. Testing the Apparatus.

One of the most satisfactory methods of testing the apparatus is to make a run with pure water in all three saturators and then compute the value of $r = \frac{p_0 - p}{p_0}$ by means of Equation 6. The result should of course be zero. In seven successive experiments of this kind in which only two saturators were employed Gordon found an average value¹ of 0.026 for 100 r . With the apparatus now in use this has been considerably reduced indicating a more perfect attainment of equilibrium between the liquid and gaseous phases during the passage of the air current. Some typical data of this kind are shown in Table I. When one recalls that the value of 100 r for a molal aqueous solution of a nonelectrolyte is about 2 it is evident that the residual errors indicated by the figures in the last column of Table I would tend to show that the error in measuring the vapor pressure lowering of a molal solution should not exceed one-fourth of 1% on the average.

¹ Gordon, *Loc. cit.*, p. 22, Table III.

TABLE I.—RESULTS WITH WATER IN ALL THREE SATURATORS.

| Duration of run. | Saturators used in calculation. | m_o . | D_m . | Volume of air aspirated. Liters. | ΔP_1 . ¹ | ΔP_2 . ¹ | ΔP_3 . ¹ | 100 r . ² |
|--------------------|---------------------------------|---------|---------|----------------------------------|-----------------------------|-----------------------------|-----------------------------|------------------------|
| 45 hrs. | 1 and 2 | 18.2417 | 0.0033 | | | | | —0.0027 |
| | | | | 789.0 | 0.18 | 0.33 | 0.50 | 0.0041 |
| 24 hrs. | 1 and 2 | 14.9147 | 0.0051 | | | | | 0.0051 |
| | | | | | | | 0.33 | 0.0025 |
| | 2 and 3 | 14.9147 | 0.0029 | | | | | 0.0036 |
| Mean value, 0.0036 | | | | | | | | |

6. The Vapor Pressures and Osmotic Pressures of Cane Sugar Solutions.

The Experimental Data.—In order that a check upon the reliability of the results obtained with our apparatus might be secured, some measurements were carried out with solutions of cane sugar for the purpose of securing a comparison with the accurate osmotic pressure data obtained by Morse. The sugar employed had been carefully purified and the measurements were made on a weight molal solution to which 0.1 of 1% of HgCl_2 was added. The results obtained are shown in Table II. The average percentage deviation of the individual results from the mean is 0.4% showing that reasonably *concordant* results can be obtained at this concentration. Their *accuracy* can be tested by calculating the corresponding values of the osmotic pressure and comparing with Morse's directly measured values for the same solution.

TABLE II.—VAPOR PRESSURE MEASUREMENTS OF WEIGHT-MOLAL SOLUTIONS OF CANE SUGAR.

| Duration of run. | Saturators used in calculation. | m_o . | D_m . | Volume of air aspirated. Liters. | ΔP_1 . | ΔP_2 . | 100 r . | Deviations. |
|------------------|---------------------------------|---------|---------|----------------------------------|----------------|----------------|--------------------|---------------------|
| 24 hrs. | 1 and 2 | 11.7458 | 0.2401 | | | | 1.974 | +0.004 |
| | | | | 509 | 0.24 | 0.29 | 0.31 | |
| | 2 and 3 | 11.7432 | 0.2375 | | | | 1.957 | —0.013 |
| 24 hrs. | 1 and 2 | 11.6451 | 0.2376 | | | | 1.965 | —0.005 |
| | | | | 504 | 0.39 | 0.48 | 0.57 | |
| | 2 and 3 | 11.6464 | 0.2389 | | | | 1.975 | +0.005 |
| 23 hrs. | 1 and 2 | 4.8408 | 0.0996 | 209 | 0.09 | 0.13 | 1.987 ¹ | +0.017 ¹ |
| Mean, 1.970 | | | | | | | | +0.008 = 0.4% |

POLARISCOPE READINGS FOR THE ABOVE SOLUTIONS.

| For the solution used in the | Before the run. | After the run. |
|------------------------------|-----------------|----------------|
| 1st run. | 356.25° | 356.00° |
| 2nd run. | 355.61° | 355.58° |

¹ The pressures here given are mean values (weighted-time-averages) and are expressed in millimeters of mercury.

² $r = (p_o - p)/p_o$.

³ Because of the small value of m_o in this run, this value was given only half-weight in the calculation of the mean.

Osmotic Pressure and Vapor Pressure Lowering.—The osmotic pressure of a solution as directly measured in such experiments as those of Morse is defined by the equation

$$\pi' = P - 1 \quad (8)$$

where P is the pressure (in atmospheres) upon the solution when osmotic equilibrium is attained. The osmotic pressure thus defined is connected with the partial vapor pressure of the solvent by the purely thermodynamic relation,¹

$$\left(\frac{\partial p}{\partial \pi'}\right)_T = -\frac{\bar{V}}{v}, \quad (9)$$

where v is the specific volume of the saturated vapor at the temperature T , and \bar{V} , the "specific solution volume" of the solvent, is the increase in volume which occurs when 1 g. of the solvent is added to an infinite amount of the solution, under the pressure P .

For saturated water vapor at 25°, we may without appreciable error assume Boyle's law for the small pressure interval here involved and write

$$v = \frac{k}{p}. \quad (10)$$

The constant k is most accurately obtained from the thermodynamic relation

$$k = \frac{L_v p}{T(\partial p / \partial T)_p} \quad (11)$$

where L_v is the latent heat of vaporization. The best available data for water when substituted in this equation give a value of k which is not appreciably different from $RT/18$ which value we shall, therefore, employ.

\bar{V} , the specific solution volume of the solvent, will in general be a function of π' . It may be calculated for any solution which contains s per cent. of solute and has the density D_P , by means of the relation

$$\bar{V} = \frac{1}{D_P} + \frac{s}{D_P} \left(\frac{dD_P}{ds} \right) \quad (12)$$

For cane sugar solutions the evaluation of \bar{V} at 25° in terms of π would strictly require a knowledge of the proper compressibility coefficients of the solutions at this temperature. No such data seem to be available but by employing those of Tait² for 12.4° an approximate calculation of \bar{V} as a function of π' may be made. In this way we find the following values:

¹ This rigorously exact relation can be written down immediately with the aid of the perfect thermodynamic engine described in a previous paper (THIS JOURNAL, 32, 467 (1910)) giving a much shorter and more direct derivation than that given by Porter for the relation between these two quantities.

² Landolt-Börnstein tables.

| | | | | | | |
|-----------------|--------|--------|--------|--------|-------|-------------|
| π | 0 | 8.44 | 16.93 | 22.16 | 26.52 | atmospheres |
| \bar{V} | 1.0029 | 1.0056 | 1.0034 | 1.0008 | 0.999 | cc. |

By integration between 0 and 27 atmospheres the average value of \bar{V} between these limits is found to be 1.003.

Equation 9, therefore, becomes

$$1.003 \, d\pi' = - \frac{RT}{18} \frac{dp}{p} \quad (13)$$

and on integration gives

$$\pi' = \frac{RT}{18.054} \left[\left(\frac{p_0 - p}{p_0} \right) + \frac{1}{2} \left(\frac{p_0 - p}{p_0} \right)^2 + \dots \right] \quad (14)$$

In Table III the values of π' calculated with this equation from the vapor pressure data of Table II are compared with the directly measured values of Morse. The agreement between the two is well within the experimental errors of the vapor pressure data and justifies the conclusion that the values obtained with our apparatus are correct within their own degree of precision.

TABLE III.—COMPARISON OF OSMOTIC PRESSURES CALCULATED FROM VAPOR PRESSURE MEASUREMENTS WITH OSMOTIC PRESSURES OBSERVED.

| 100 r. | Osmotic pressure calculated. | Osmotic pressure observed (Morse). |
|--------------------|---------------------------------|---------------------------------------|
| 1.974 | 27.01 | 27.030 |
| 1.957 | 26.77 | .. |
| 1.965 | 26.88 | .. |
| .975 | 27.02 | 27.076 |
| 1.987 | 27.19 | .. |
| Mean, | 27.0 | 27.05 |
| Average deviation, | 0.11 | |
| % deviation, | 0.4 | |

7. Discussion of the Method.

The results obtained with our apparatus indicate that values of $\frac{p_0 - p}{p_0}$ of the order of magnitude of 0.02 can be measured with an accuracy of better than 0.5% in a 24-hour run. This seems to be about ten times better than the best values recorded for the dynamic method as usually carried out.¹

The experiments of Berkeley, Hartley and Burton,² however, who employed the differential method of Ostwald-Walker also gave closely concordant results. They worked with calcium ferrocyanide solutions in small saturators of the same general form as that shown in Fig. 3 and their method differed from ours only in the fact that the air entered the system perfectly dry and the losses in weight of the two saturators were determined by weighing them directly. It is difficult to directly compare the degree of accuracy which they obtained with that given by our ap-

¹ Cf. Gordon's discussion, *Loc. cit.*, p. 23.

² *Loc. cit.*

paratus because they worked entirely with stronger solutions and only two measurements are recorded for any one concentration. Their most dilute solution gave $\frac{p_0 - p}{p_0} = 0.032$, the two determinations differing by only 0.2%. Similarly for stronger solutions, the differences between the two determinations were for $\frac{p_0 - p}{p_0} = 0.054$, $d = 0.1\%$; for $\frac{p_0 - p}{p_0} = 0.065$, $d = 0.03\%$; for $\frac{p_0 - p}{p_0} = 0.084$, $d = 1.0\%$. The *percentage* accuracy should, of course, increase rapidly with increase in the relative lowering measured and although we have as yet made no careful measurements with solutions in which $\frac{p_0 - p}{p_0}$ exceeded 0.02, the results obtained by Berkeley, Hartley and Burton as far as a comparison is justified seem to show in general a degree of concordance of the same order as that given by our apparatus. Their experiments were made at 0° , and the duration of a run was about *three days*.

In the static method for measuring vapor pressure lowering as perfected by Frazer and Lovelace an accuracy of 0.001 mm. is claimed. This would correspond to an accuracy of 0.2% on the value of $\frac{p_0 - p}{p_0}$ for a weight molal solution at 25° and is, therefore greater than that obtained in our experiments with the cane sugar solutions, but of the same order of accuracy as that indicated by the data recorded in Table I. By extending the time of run over several days instead of one, more complete equilibrium could perhaps be obtained with our apparatus but the possible increase in accuracy which might thus be secured has not in most cases seemed worth the additional expenditure of time.

In Frazer and Lovelace's apparatus a minimum of about eight days seems to be required for the attainment of equilibrium and its final measurement, but their results at the end of that period appear to be very accurate, which is more than can be said of any previous attempts to use the static method, and they are to be congratulated upon their success where so many others have failed. We are at present engaged in measuring solutions of mannite at 25° and 35° and as these authors appear to be working with the same solutions we may hope to obtain a direct comparison of results by the two methods for the same solutions.

URBANA, ILLINOIS.

NOTE.

Nichrome Gauze.—Many questions have been asked concerning this gauze, designed in 1911 at Amherst College and since distributed to many of the New England laboratories. It had been the custom to supply

student near-by paper mills, but on the introduction of water-gas, the brass wire deteriorated rapidly over the Bunsen flame. The nichrome wire was supplied by the Driver Harris Company, of Harrison, New Jersey, to the weavers, Messrs. Howard and Morse, 45 Fulton Street, New York, and proved all that was

desired. In fact, the raw edge of the gauze may be held for a long time in the flame of a blast lamp without any evidence of deterioration of the fine wire; and in the past three years no single gauze has been returned as damaged at the end of a year's service in the laboratories.

The first cost of these gauzes, compared with that of brass wire, is quite high. The standard gauze (5" × 5") in the first experimental order cost 55 cents each. Later, a larger order was sent amounting to nearly \$400 and the cost of each gauze was reduced to about 25 cents each. As the nichrome seems to last indefinitely, the first cost is gradually eliminated and in the end

this gauze becomes cheaper than brass; and at the same time the need of sending a new order each year is eliminated.

The specifications as finally drawn were determined by the following considerations. The British Commission on the Davy Lamp determined that, in order to permit flame to pass, spaces should be at least 0.025" on a side. The following space equivalents are given for various sizes of wire and mesh per inch.

| B and S gauge. | 30 mesh. | 28 mesh. |
|----------------|----------|----------|
| 26 | 0.0175 | 0.0198 |
| 27 | 0.0191 | 0.0215 |
| 28 | 0.0207 | 0.0231 |
| 29 | 0.0220 | 0.0244 |
| 30 | 0.0233 | 0.0257 |

The choice of No. 30 wire was made because this gives a particularly smooth and flexible gauze; and this was combined with No. 30 mesh as the space equivalent for this combination is nearest to the danger line. With thicker wire or smaller mesh the price advances about 10% for each step. The best gauze is one which is sufficiently open to allow the passage of the maximum heat without allowing flame to pass. The gauze produced proved very satisfactory, allowing—to be exact—a very slight flickering flame about $\frac{1}{8}$ " above the gauze (probably due to the difference in heat conductivity between copper and nichrome) but not enough to damage a glass beaker placed above; and allowing, at the same time, nearly all the heat of the lamp to pass.

The large order of nearly 1600 gauzes was quickly subscribed and no more now remains than sufficient to supply this laboratory; but if a few laboratories care to club together, the same or better terms could doubtless be secured from the weavers, who have kindly assisted us with advice and coöperation in the production of this new article. When one considers the possibility of damage by students' use, the subjection of the red-hot gauze to accidental flooding with concentrated acids or alkalies, the record of not a single damaged gauze in three years is quite remarkable. Satisfaction with this innovation increases with the lapse of time.

AMHERST COLLEGE,
Dec. 7, 1914.

ARTHUR JOHN HOPKINS.

CHLOROPHYLL.

By RICHARD WILLSTÄTTER.

Received December 23, 1914.

The Method of Investigation.¹

Some years ago, chlorophyll was unknown as a substance in a chemical respect. It was doubtful whether there was one chlorophyll or several pigments related to each other, or a great number of green leaf dyestuffs. The first questions of the analysis were unsolved; it was yet undecided which elements belonged to the chlorophyll molecule. Through the investigations of F. Hoppe-Seyler,² E. Schunck and L. Marchlewski,³ and M. Nencki,⁴ the chief fact found was that the decomposition of chlorophyll leads to pyrrol derivatives which are related to the derivatives from blood pigment.

After some investigations of Hoppe-Seyler⁵ and A. Gautier⁶ (1879) chemists no longer attempted to isolate chlorophyll, for this appeared impossible principally on account of the changeability, the chemical indifference and the easy solubility of the dyestuff diluted, as it was, with so many colorless and yellow accompanying substances. But it was possible, without investigating chlorophyll itself, to deduce the peculiarities of its constitution from the consideration of the derivatives which are obtained by the reactions with acid and alkali.

¹ A more detailed report is given by R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," from the Kaiser Wilhelm-Institut für Chemie, Berlin, 1913 (J. Springer).

² *Z. physiol. Chem.*, 3, 339 (1897); 4, 193 (1880); 5, 75 (1881).

³ Complete abstracts of the numerous researches performed by E. Schunck and L. Marchlewski are published in three monographs of L. Marchlewski, "Die Chemie des Chlorophylls," Hamburg, 1895; chapter "Chlorophylle," in Roscoe-Schorlemmer-Brühl, Vol. VIII, 848 (1901); "Die Chemie der Chlorophylle," Braunschweig, 1909.

⁴ *Ber.*, 29, 2877 (1896); M. Nencki and J. Zaleski, *Ibid.*, 34, 997 (1901); M. Nencki and L. Marchlewski, *Ibid.*, 34, 1687 (1901).

⁵ *Z. physiol. Chem.*, 3, 339 (1879).

⁶ *Compt. rend.*, 89, 861 (1879).

If alkali hydroxide is allowed to act on chlorophyll, it is changed into salts of chlorophyll, green color. From the neutral chlorophyll, an acid is obtained which forms water-soluble salts. Therefore, without a considerable optical change by the reaction with alkalies, a component which was bound with an acid group is hydrolytically split off. This reaction is the saponification of an ester.

There is another part of the molecule against which the gentle action of acid is directed. The chlorophyll color changes thereby to an olive, at the same time the fluorescence is weakened, a salt-forming group is not formed, showing that saponification is avoided. Therefore, in the splitting with acid, it is possible to preserve and to find in the products of hydrolysis that component which is separated by alkalies, and conversely, the alkali derivatives of the dyestuff must likewise exhibit a characteristic atomic group, which is destroyed with extraordinary ease by acid. According to this guiding idea,¹ it was possible, before chlorophyll itself was known, to determine its characteristics from the analysis of the decomposition products formed by acid and alkali, and indeed so completely, that the analysis at the end gave nothing new when we succeeded in preparing the natural dyestuff pure.

The chlorophyll-green acids, the chlorophyllins, which are formed by alkaline hydrolysis in an alcoholic extract of the leaves, are decomposed very easily, but they can be separated successfully in a fairly pure condition from a mixture with other products of the saponification. They were taken up from their ethereal solution by disodium phosphate and liberated again from it by monosodium phosphate. By analysis, they have been shown to be magnesium compounds.² In them the metal is bound to the nitrogen, the linkage being of a complex nature. The magnesium-containing group is very sensitive towards acids, but it is uncommonly stable against alkalies. It remains intact consequently even in the more far-reaching transformations of the molecule in which the carboxyl groups are split off, one after the other. The presence of magnesium has been proven and the assumed manner of its binding has found confirmation in the results of the continued action of alkalies,³ particularly by the decomposition of the chlorophyllins on heating with concentrated alcoholic alkali to 240°. This yields a series of well-crystallizing, beautifully colored, intensely fluorescent decomposition products, the so-called phyllins with three, two and finally one carboxyl group. All these compounds, of which a number have received names such as glauko- and rhodophyllin, from

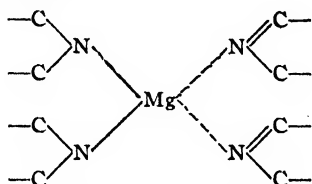
¹ R. Willstätter and F. Hocheder, *Ann.*, **354**, 205 (1907).

² R. Willstätter, *Ibid.*, **350**, 48 (1906).

³ R. Willstätter and A. Pfannenstiel, *Ibid.*, **358**, 205 (1907); R. Willstätter and H. Fritzsche, *Ibid.*, **371**, 33 (1909); R. Willstätter and M. Utzinger, *Ibid.*, **382**, 129 (1911); R. Willstätter, M. Fischer and L. Forsén, *Ibid.*, **400**, 147 (1913).

their beautiful blue and red color, and of which we have prepared a dozen as homogenous crystals, contain magnesium and at the same time are free acids.

The assumption that a complex is formed by magnesium with the nitrogen atoms has been doubted in the past years, but recently its correctness was proven beyond doubt by the decomposition of the phyllins to the carboxyl-free fundamental substance, the aetiophyllin,¹ the composition of which is expressed by the formula $C_{31}H_{34}N_4Mg$. In consequence of the diminution in the size of the molecule, the ash content has risen to 8% of magnesium oxide. There are only nitrogen-containing groups available, which bind the magnesium with two valencies and fasten it in a complex with secondary valencies. The constitution of the remaining phyllins is analogous, and their oxygen atoms have no part in the binding of the metal complex:



The magnesium content of chlorophyll is constant.² And this has been found, without exception, in land and water plants of the most different classes. For a long time it has been known that magnesia is indispensable as a mineral constituent of plants, but now, for the first time, the definite function of the metal has been established. Inasmuch as it is not a case of catalytic influence, such as is ascribed to iron for chlorophyll formation, but a stoichiometric participation of the magnesium in the building up of chlorophyll, the attention of the agricultural chemists should be directed to the question whether magnesia is provided by nature in sufficiency for the useful plants. The effect of an addition of magnesium salt on the chlorophyll formation and growth with different kinds of cultures was investigated a short time ago by E. Mameli³ in the Botanical Institute at Pavia and a favorable influence of added magnesium was found.

All the phyllins lose magnesium by the action of mineral acids, as well as by acetic acid; the carboxylic acids of the phyllin series pass, thereby, into polybasic or monobasic amino acids which display characteristic basic properties besides the acid ones. They form a natural group with the phylloporphyrin discovered by F. Hoppe-Seyler,⁴ later investigated,

¹ R. Willstätter and M. Fischer, *Ann.*, 400, 182 (1913).

² R. Willstätter and A. Pfannenstiel, *Ibid.*, 358, 205 (1907); R. Willstätter and H. J. Page, *Ibid.*, 404, 237 (1914).

³ *Atti della Soc. Ital. per il Progr. d. Scienze*, 5, 793 (1911); *Atti dell' Ist. Bot. dell' Università di Pavia*, [2] 15, 1 (1912).

⁴ *Z. physiol. Chem.*, 4, 193 (1880).

but not obtained in a pure condition, by E. Schunck.¹ Therefore, they are named porphyrins and that prefix is added which belongs to the corresponding phyllin. From the oxygen-free aetiophyllin, the simplest porphyrin, aetioporphyrin, of the formula $C_{31}H_{36}N_4$ is formed.

Analogous to the behavior of the phyllins towards acid is the action of acids on the solutions of chlorophyll itself. For the investigation of this reaction, the observation was fundamental that, by gentle decomposition with oxalic acid, a chlorophyll derivative, the so-called phaeophytin which is not readily soluble in alcohol and free from colorless and yellow accompanying substances, is precipitated almost quantitatively from an alcoholic extract of the leaves. It no longer contains magnesium, and the splitting off of the metal is the only change which has occurred, if the preparation of the plant material, the extraction, and the treatment with acid is made with all the precautions which are suggested by the experience of this work.

The phaeophytin recalls to mind the substances which F. Hoppe-Seyler² in 1879 and at the same time A. Gautier³ obtained as products of the unintentional decomposition of chlorophyll by the plant acids, contained in the extracts. The old preparations,⁴ however, were not free from accompanying substances and not intact in the easily changeable atomic groups of the dyestuff molecule. Hoppe-Seyler found in such a substance, the chlorophyllan, a phosphorus content of 1.4% and was thereby led to the supposition that chlorophyll might belong to the lecithins. The hypothesis, cautiously expressed by Hoppe-Seyler, is ardently upheld by J. Stoklasa⁵ up to the present day, who states to have found phosphorus and potassium in chlorophyll, and indeed more phosphorus than in lecithin. This experience cannot be corroborated.⁶ The long and uncertain way by which chlorophyllan used to be obtained is now replaced by a method which permits us to separate the chlorophyll of any origin as a pure derivative. It can now be obtained on a kilogram scale by the ordinary means of the laboratory; the meal of dried common nettle leaves is a suitable starting material (yield 4 to 6 g. phaeophytin from 1 kg.).

The phaeophytin is a wax-like substance without acid properties and of a weak basic nature. As regards the color of its solutions, it is quite different from chlorophyll, but the similarity of this decomposition product to chlorophyll appears as soon as a metal is introduced into the molecule,

¹ *Proc. Roy. Soc.*, 50, 302 (1891); E. Schunck and L. Marchlewski, *Ann.*, 284, 81 (1894); *Proc. Roy. Soc.*, 57, 314 (1895).

² *Z. physiol. Chem.*, 3, 339 (1897).

³ *Compt. rend.*, 89, 861 (1879).

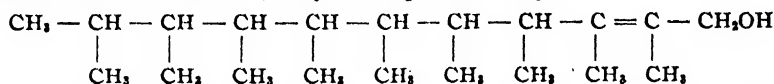
⁴ See R. Willstätter and M. Isler, *Ann.*, 390, 287 and 337 (1912).

⁵ *Ber. Deutsch. bot. Ges.*, 26, 69 (1907) and 27, 10 (1909); J. Stoklasa, J. Sebor and E. Senft, *Beihfte z. Bot. Zentralbl.*, 30, Erste Abt., Heft 2, 167 (1913).

⁶ R. Willstätter and E. Hug, *Ann.*, 380, 177, 209 (1911).

in which it becomes bound as a complex.¹ Many metals enter very easily, for example, copper and zinc by the action of their acetate salts on the alcoholic solution of phaeophytin. The complex formation is a phenomenon so evident that the smallest traces of certain metals can be shown by the aid of chlorophyll derivatives. It was much more difficult to reintroduce the magnesium on account of the sensitiveness of the magnesium complex to acids. This has been attained² finally by the action of the Grignard solutions, for example, of magnesium methyl iodide on phaeophytin or on porphyrins. Another method, namely, the action of magnesium oxide and alkali in the heat, is not applicable for the reformation of chlorophyll on account of its instability towards alkali, but is very suitable for the formation of the phyllins from the porphyrins. In the same manner, iron can be introduced into the porphyrins by heating with methyl alcoholic potassium hydroxide and iron oxide.

Phaeophytin³ behaves like a wax upon saponification with alkalis and produces, besides high molecular nitrogen-containing acids with 34 atoms of carbon, a nitrogen-free alcohol with twenty carbon atoms. It has been isolated and called phytol. It has the formula $C_{20}H_{39}OH$ and is an unsaturated primary alcohol with an open chain of carbon atoms. Investigations⁴ concerning its decomposition have made it probable that its carbon skeleton has many side-chains and that it contains many methyl groups. For its structure, the following constitutional formula, which is hypothetical in its details, may serve provisionally:



It is probable that relations exist between isoprene, the well-known building stone of the terpenes and caoutchouc, and this alcoholic component of chlorophyll.

Consequently the chlorophyll derivative, formed by acid, has yielded the information which was sought concerning the chief transformation which the alkalis produce upon the molecule of chlorophyll; they saponify the phytol ester group. The action, however, is not limited to this group; for the phaeophytin, and as a result the chlorophyll, contains further a $COOCH_3$ group which also is decomposed by the hydrolysis.

Phytol is of general occurrence⁵ in nature, amounting to one-third of

¹ R. Willstätter and F. Hocheder, *Ann.*, **354**, 208 (1907); R. Willstätter, A. Stoll and M. Utzinger, *Ibid.*, **385**, 180 (1911).

² R. Willstätter and L. Forsén, *Ibid.*, **396**, 180 (1913).

³ R. Willstätter and F. Hocheder, *Ibid.*, **354**, 205 (1907).

⁴ R. Willstätter, E. W. Mayer and E. Hüni, *Ibid.*, **378**, 73 (1910); O. Schuppli, Dissertation, Zürich, 1912.

⁵ R. Willstätter, F. Hocheder and E. Hug, *Ann.*, **371**, 1 (1909); R. Willstätter and A. Oppé, *Ibid.*, **378**, 1 (1910); R. Willstätter and H. J. Page, *Ibid.*, **404**, 237 (1914).

the weight of chlorophyll, and the phytol occurs constantly as a component of chlorophyll. This knowledge was obtained in an indirect manner by working up different plants. In the beginning, the phaeophytin preparations of different origin showed considerable fluctuations. The phytol content never exceeded 33% but not infrequently remained below that figure and in many cases sank to zero. Now it has been found that just those plants containing a chlorophyll poor in phytol proved to be an excellent material for the isolation of chlorophyll in a peculiar form of beautiful crystals.¹ These crystals were the same which the Russian botanist J. Borodin² discovered under the microscope in 1881. Borodin observed the formation of crystals under certain conditions, namely, when drying alcohol-moistened sections of leaves. He left the question open, however, whether these crystals originated from chlorophyll or from transformed chlorophyll. N. A. Monteverde³ continued the investigation and isolated such crystals in a small quantity in order to characterize them spectroscopically. But the substance had not been analyzed and chemically investigated. In the monographs concerning chlorophyll, Borodin's research was not mentioned. The discovery, therefore, remained useless until it was made a second time in the chemical laboratory. In 1907, I obtained, together with Benz, the so-called crystallized chlorophyll on a large scale, but at a time when the analysis of chlorophyll had been already completed by indirect methods. The production of crystallized chlorophyll on a preparative scale was of special value for investigations, until it became possible to separate the natural dyestuff itself in a pure condition.

The formation of the crystallized compound and the corresponding deficiency of phytol could be explained only by the observation⁴ that by rapid extraction of many leaves the phytol content is normal. But by slow extraction, when the extract remains in contact with the meal of dried leaves for some time, it is too low. According to Willstätter and Stoll,⁵ the chlorophyll in the green plant parts is accompanied by an enzyme, the chlorophyllase, belonging to the esterases. This is not inactive in alcoholic media, as is generally assumed for enzymes, but it causes the displacement of the phytol by the alcohol applied as a solvent and thereby effects alcoholysis of the chlorophyll. The enzyme occurs pretty generally; for example, it is contained in large quantity in *Galeopsis* and *Heracleum*, but its quantity appears to fluctuate within wide limits. After the dynamics of this enzyme reaction had been sufficiently studied,

¹ R. Willstätter and M. Benz, *Ann.*, **358**, 267 (1900).

² *Botan. Z.*, **40**, 608 (1882).

³ *Aceta Horti Petropolitani*, **13**, Nr. 9, 123 (1893).

⁴ R. Willstätter and A. Oppé, *Ann.*, **378**, 1 (1910).

⁵ *Ann. Chem.*, **378**, 18 (1910).

extensive application of the action of chlorophyllase was made for preparative purposes. There is no longer anything accidental about the preparation of crystallized chlorophyll. From fresh, as well as from dried leaves, almost the total chlorophyll can be separated in the form of the ethyl or methyl compound (ethyl or methyl chlorophyllide) or through hydrolysis in the form of the corresponding free carboxylic acid, the chlorophyllide.¹ The reversal of the hydrolysis, the partial synthesis² of chlorophyll from the two components, has also been carried out, namely, from chlorophyllide with the alcohol phytol by esterification under the catalytic influence of chlorophyllase. The usual methods of ester formation could not be applied in this case on account of the sensitiveness of chlorophyll.

Inasmuch as the phaeophytin is the most suitable form of chlorophyll for investigation as well as for the comparison of the leaf green from different plants, the characterization of chlorophyll, apart from the determination of magnesium and phytol, requires above all the knowledge of the nitrogen-containing acids which result, besides the phytol, upon saponification of phaeophytin. Although this is a pure chlorophyll substance, it is not a homogeneous compound; its acid component contains substances which differ in basic properties and color.³ In the beginning, the investigation led to a great number of such decomposition products which form two groups; the one, phytochlorins, olive-green in indifferent solution, the other, phytorhodins, beautifully red. On account of their great number, the single compounds are designated with group names and letters added to them.

We would have scarcely succeeded in throwing light on the mixture of complicated composition which is met by the first transformations of chlorophyll if the basic nature of the decomposition products, in their unprecedented differentiation, had not placed in our hands a never-failing method⁴ for the determination and separation of chlorophyll derivatives. This method (Willstätter and Mieg) depends on the different distribution of these dyestuffs between ether and hydrochloric acid. The proportion in which these bases are distributed between ether and dilute acids varies in a most unusual manner with the acid concentration. The concentration of the acid, which under ordinary conditions extracts a large quantity of the substance from ether, is so important for preparative purposes that particular weight must be attached to it. We call "the

¹ R. Willstätter and A. Stoll, *Ann.*, 387, 317 (1912).

² R. Willstätter and A. Stoll, *Ibid.*, 380, 148 (1911).

³ R. Willstätter and F. Hocheder, *Ibid.*, 354, 212 and 242 (1907); see M. Tswett, *Biochem. Z.*, 5, 6 (1907); 6, 373 (1907); 10, 404 (1908); *Ber.*, 41, 1352 (1908).

⁴ R. Willstätter and W. Mieg, *Ann.*, 350, 1 (1906); R. Willstätter, M. Fischer and L. Forsén, *Ibid.*, 400, 151, 178 (1913); R. Willstätter and M. Fischer, *Z. physiol. Chem.*, 87, 439 (1913); R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," Chap. XIV.

hydrochloric acid number" the percentage content of that acid which by shaking removes approximately two-thirds of the dissolved substance from an equal volume of an ethereal solution.

HYDROCHLORIC ACID NUMBERS.

| | Traces are extracted by acid of per cent. | Almost entirely extracted by acid of per cent. | Hydrochloric number. |
|-----------------------------------|---|--|-----------------------------------|
| Phaeophytin <i>a</i> | 25 | 32 | 29 |
| Phaeophytin <i>b</i> | 30 | .. | 35 |
| Methylphaeophorbid <i>a</i> | 13 | 18 | 16 |
| Methylphaeophorbid <i>b</i> | 17 | 23 | 21 |
| Phaeophorbid <i>a</i> | 12 | 17 | 15 |
| Phaeophorbid <i>b</i> | 16 | 22 | 19 ¹ / ₂ |
| Phytochlorin <i>e</i> | 1 ¹ / ₂ | 4-5 | 3 |
| Phytochlorin <i>f</i> | 7 | 12 | 10 |
| Phytochlorin <i>g</i> | 8 | 12-13 | 10-11 |
| Phytorhodin <i>g</i> | 6 | 11 | 9 |
| Phytorhodin <i>i</i> | 11 | 20 | 15-16 |
| Phytorhodin <i>k</i> | 9 | 18 | 14-14 ¹ / ₂ |
| Glaukophorphyrin..... | 2 | 6 | 4-5 |
| Cyanophorphyrin..... | 1 | 5 | 4 |
| Rhodophorphyrin..... | 2 | 4 | 3 |
| Rubiporphyrin..... | 2 ¹ / ₂ | 6 ¹ / ₂ | 4 ¹ / ₂ |
| Pyrrorphyrin..... | 1 ¹ / ₂ | 3 | 1 ¹ / ₂ |
| Phylloporphyrin..... | 1 ¹ / ₁₀ | 1 ¹ / ₂ | 2 ³ / ₄ |
| Aetioporphyrin..... | 1 | 4 | 3 |

The decomposition products of phaeophytin, occurring in mixtures, were therefore separated by fractionation of their ethereal solution with hydrochloric acid of varying concentration. But the appearance of complicated mixtures was only a result of certain transformations, which the chlorophyll, being very changeable in alcoholic solution, underwent under the experimental conditions, as, for example, too slow extraction or too slow precipitation with acid. The preliminary treatment of the plant material and particularly its extraction and the treatment of the extract with acid had to be improved and to be made more uniform. By looking for the causes of the changes appearing in the solutions and by learning to avoid them, the differences between our preparations have become less frequent and more insignificant and we have finally succeeded in obtaining two, and only two, well-crystallizing and characteristic decomposition products from phaeophytin:¹ Phytochlorin *e* of the composition $C_{34}H_{34}O_8N_4$ and phytorhodin *g* of the composition $C_{34}H_{34}O_7N_4$.

Phytochlorin *e* is a tricarboxylic acid with two free carboxyl groups and one bound as a lactam. Phytorhodin *g* is a tetracarboxylic acid; of its carboxyl groups only two or three are found in a free condition.

The common appearance of a green and red decomposition product

¹ R. Willstätter and M. Isler, *Ann.*, 380, 154 (1911); R. Willstätter and M. Utzinger, *Ibid.*, 382, 129 (1911); R. Willstätter and M. Isler, *Ibid.*, 390, 269 (1912).

by the subsequent hydrolysis of chlorophyll with acid and alkali opened up an important question.¹ Is it caused by the decomposition of a large molecule into two fragments? As an argument against this we find the molecular weight of phaeophytin to be of similar magnitude to that of phytochlorin and phytorhodin. Then again, it might be conceivable that one of the decomposition products represents an earlier, the other a subsequent step of decomposition. But phytochlorin and phytorhodin cannot be converted into each other, and they are formed in quite definite weight proportions. It followed, therefore, from the formation of phytochlorin *e* and phytorhodin *g* that phaeophytin, and consequently chlorophyll, is a mixture of two components from which the one furnishes phytochlorin *e* by decomposition, the other phytorhodin *g*. On this basis, we have succeeded in obtaining the separation of the components from the mixture by physical and chemical means.

One method² which can be applied with chlorophyll solutions, with crystallized chlorophyll and with phaeophytin, consists in the rearrangement of the given proportion by unequal distribution of the dyestuff between several solvents, immiscible with one another; for example, water containing methyl alcohol with petroleum ether or, in the case of the difficultly soluble phytol-free compounds, methyl alcohol with ether-petroleum ether. This rearrangement of the relation of the components can be repeated and so utilized by numerous repetitions of the operations that, finally, the two components of the magnesium-bearing free dyestuffs are in pure condition.

The other method,³ which of course is only applicable with magnesium-free compounds, consists in the fractionating with hydrochloric acid, according to the method of Willstätter and Mieg. The phaeophytin is so weak a base and so sensitive in its phytol-ester group toward hydrolytic agents, that this separation was not obvious and offered particular obstacles. It served its purpose, nevertheless, and confirmed the results of the first method of separation.

These results have corroborated a view which G. G. Stokes⁴ expressed as early as 1864, unfortunately in only a few short words. Stokes recognized chlorophyll spectroscopically as a mixture and he endeavored to separate it by distribution between alcohol and carbon disulfide, a method subsequently rediscovered and developed by H. C. Sorby⁵ and G. Kraus,⁶

¹ R. Willstätter and M. Isler, *Ann.*, 380, 154 (1911); 390, 269 (1912).

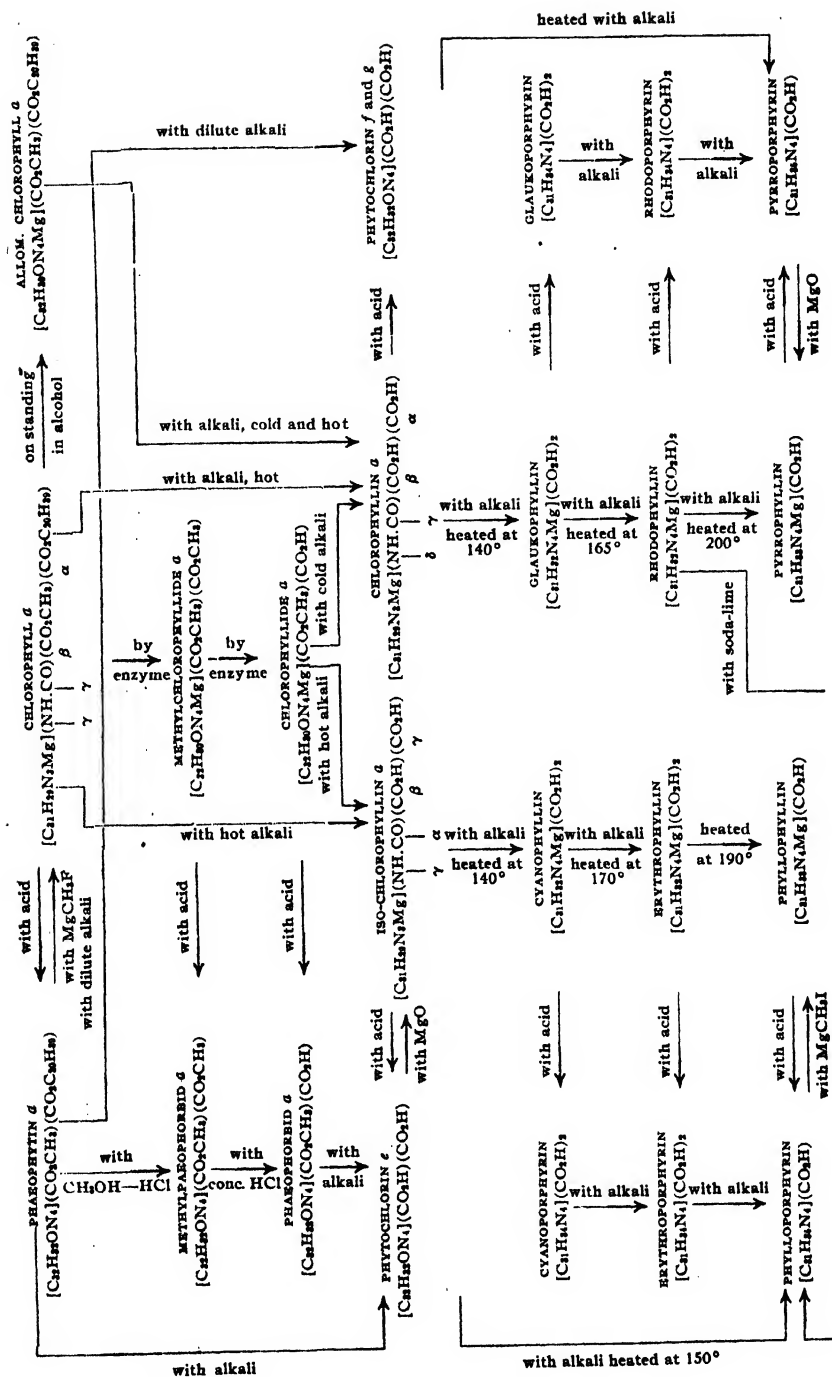
² R. Willstätter and M. Isler, *Ibid.*, 390, 269 (1912); R. Willstätter and A. Stoll, *Ibid.*, 387, 317 (1911) and "Untersuchungen über Chlorophyll," Chap. VI.

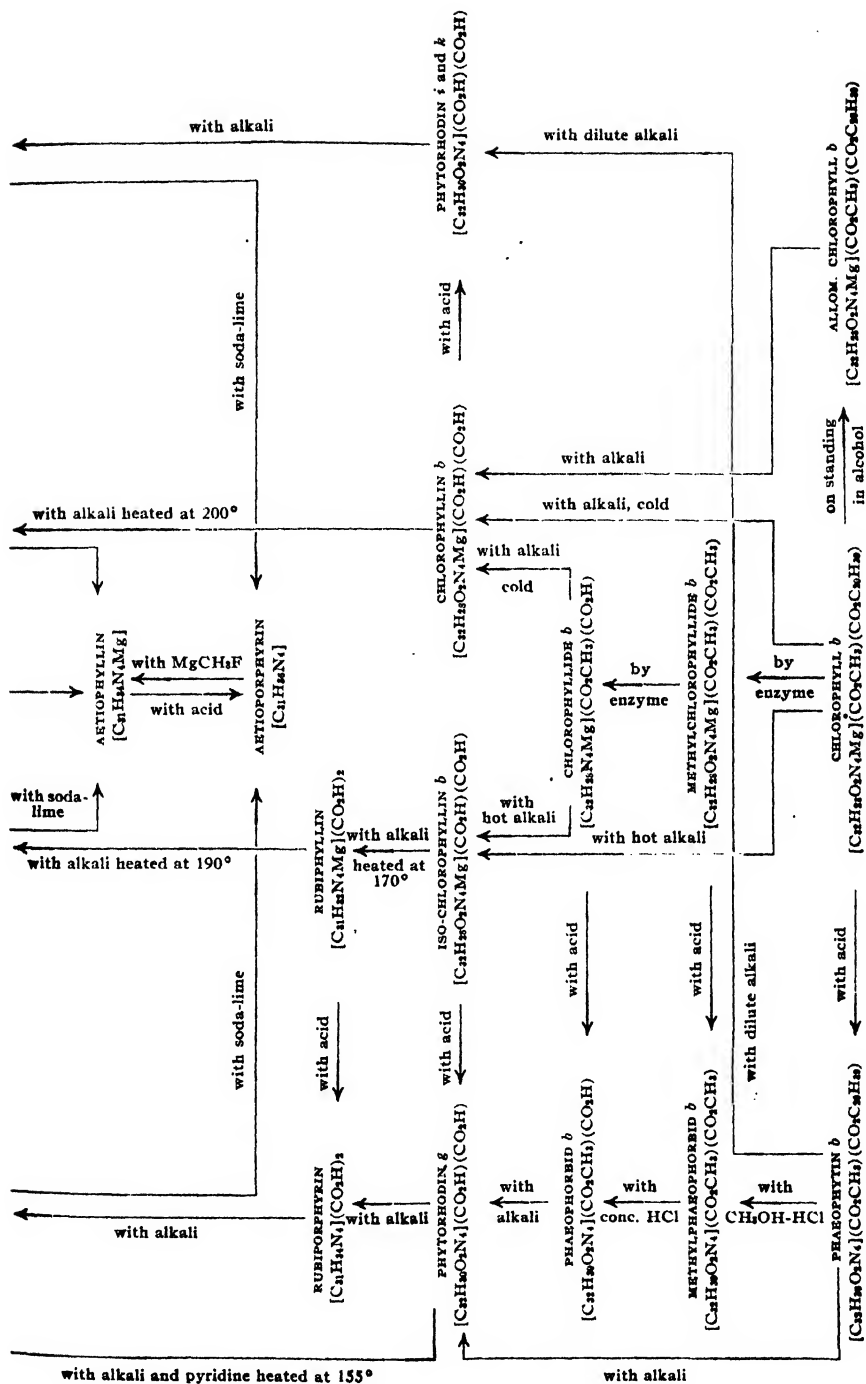
³ R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," Chap. XV.

⁴ G. G. Stokes, *Proc. Roy. Soc.*, 13, 144 (1864).

⁵ H. C. Sorby, *Ibid.*, 15, 433 (1867); 21, 442 (1873); *Quarterly Journ. of Microscopical Science*, 11, 215 (1871); *Ibid.*, 8, 64 (1871).

⁶ G. Kraus, *Zur Kenntnis der Chlorophyllfarbstoffe und ihrer Verwandten*, Stuttgart, 1872.





and much applied since then, particularly to show that yellow pigments accompany the green dyestuff. Recently, the botanist M. Tswett¹ in Warsaw has confirmed in a new, original way the view of Stokes, namely, by a separation of the natural pigment on an analytical scale by means of fractional adsorption from its solutions. It was impossible up to the present time, however, to find whether the dyestuff had changed or not by the extraction and during the following manipulations. Such changes occur easily and explain considerable errors which can be found in the work of Stokes, Sorby and Tswett. According to Stokes,² Sorby³ and Tswett,⁴ a third chlorophyll component occurs as a pigment of *Phaeophyceae*. An investigation⁵ of the pigments of seaweeds, carried out recently, has led to the result that the chlorophyll of this algae is identical with that of land plants, with the exception that component *b* is reduced in quantity. The supposed third chlorophyll dyestuff was in fact a decomposition product of chlorophyll.

Whether the chlorophyll molecule remains intact in its details must be tested by decomposition to the typical splitting products (phytochlorin *e* and phytorhodin *g*). This characterization of the constituents of the leaf-green was the condition for the final isolation of the chlorophyll in an unchanged and pure state in form of a mixture or as individual components.

Isolation of Chlorophyll and Separation into Its Components.

The isolation of chlorophyll (Willstätter and Hug, 1911) was controlled by the colorimetric determination of the degree of purity of its solutions and depended on systematic increase of the purity in the course of a "un-mixing process," in which the distribution of the substances, contained in the extracts, between several solvents is applied in a particular manner, in order to separate the yellow and, still more, the colorless substances accompanying the chlorophyll. Solutions of about 70% chlorophyll result by the un-mixing method from the extracts which, in consequence of the great quantity of accompanying colorless substances, contain only 8–16% chlorophyll. Then, finally, an unexpected observation aided in the solution of the problem. When the chlorophyll has reached a certain degree of purity, it is still easily soluble in alcohol containing petroleum ether but, surprisingly, no longer soluble in pure petroleum ether. If the ethyl or methyl alcohol is removed by washing, the chlorophyll is precipitated and it can be purified by further precipitations from ether by petroleum

¹ *Ber. Deutsch. bot. Ges.*, 44, 1125 (1911); "Die Chromophylle in der Pflanzen- und Tierwelt," Warsaw, 1910 (Russian).

² *Proc. Roy. Soc.*, 13, 144 (1864).

³ *Ibid.*, 21, 442 (1873).

⁴ *Ber. Deutsch. bot. Ges.*, 24, 235 (1906).

⁵ R. Willstätter and H. J. Page, *Ann.*, 404, 237 (1914).

ether. In the beginning, this procedure¹ was laborious and the yield was small. In newer researches with A. Stoll,² I have perfected the procedure by variations in the methods of extraction and separation.

The materials for our work on a large scale are mostly dried and pulverized leaves. It has been shown that a considerable water content of the solvent essentially facilitates and accelerates the extraction of the

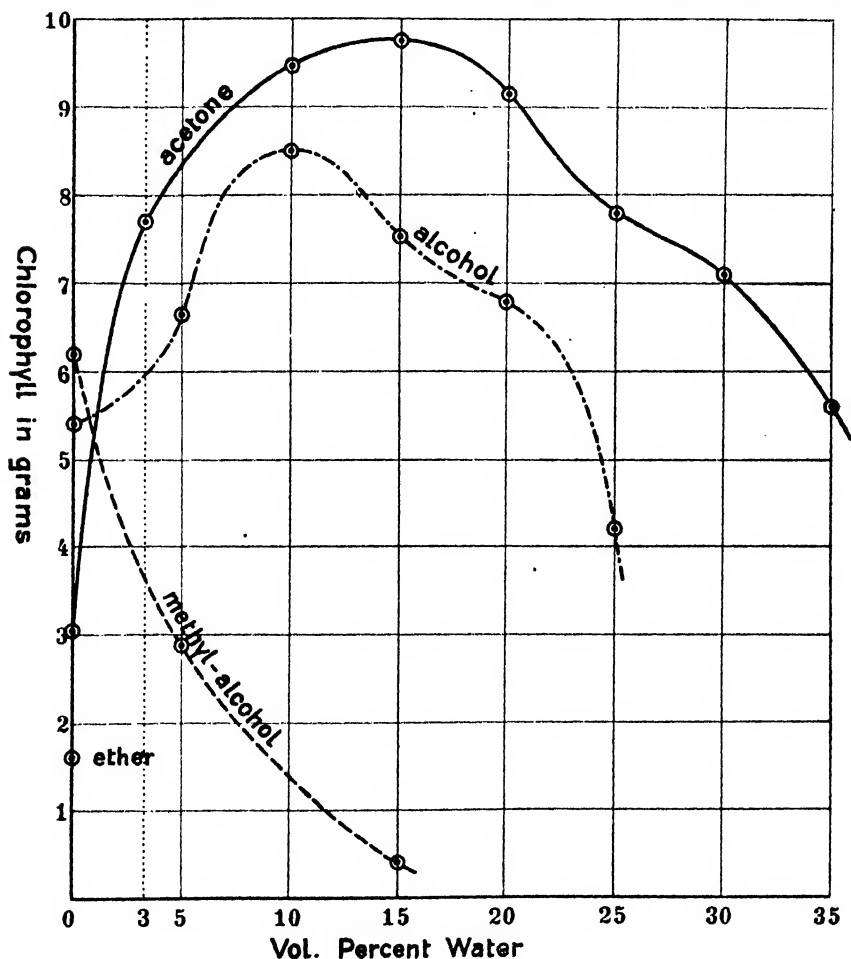


Fig. 1.

total leaf dyestuff. The pigments in the chloroplasts, even after drying, are found in a colloidal condition and are difficultly soluble. They are coagulated by a solvent which dissolves salts out of the material and are

¹ R. Willstätter and E. Hug, *Ann.*, 380, 177 (1911).

² R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," Chaps. III and VI.

therefore made more easily soluble. Besides, the quantity of the accompanying substances going into solution is increased and it is no longer the solvent itself but a mixture with the accompanying substances which becomes the particular means of extraction for the green of the leaf and, indeed, one so excellent, that the dyestuffs are quickly, easily and almost quantitatively extracted by it. It appears as if actually the whole chloroplast substance was carried off by the solvent with suitable water content.

The best solvents are 85 to 90% alcohol and especially 80 to 85% acetone; the following figures show the influence of the water percentage on the chlorophyll content of the extract.

At the present time we can isolate pure chlorophyll in a few hours without much trouble from a few kilograms of dried leaves with a yield of about 80% of the quantity, that is, about 6.5 g. from a kg. of dried leaves. The procedure can also be carried out with fresh leaves, and likewise, as in the whole course of the work, no difference between the freshly plucked and the dried leaves resulted in the production of the chlorophyll preparations and in their properties. In a lecture hour, a quarter of a gram of pure chlorophyll can be isolated from a quarter of a kilogram of fresh common nettles. The leaf dyestuff can be isolated, at present, as easily as any kind of a plant constituent, as an alkaloid or a sugar.

With our methods of separation the two components are divided in an unequal manner between methyl alcohol and petroleum ether. By systematic fractionating, the rearrangement of the proportion of the components to each other is continued so far that finally the two components¹ result quite homogeneous from the mixture. The one component, chlorophyll *a*, is bluish green, the second, chlorophyll *b*, yellowish green. Their composition, in spite of their optical difference,² is very similar. The distinction is due to a different degree of oxidation. With the chlorophyll itself, we find confirmed what the formulae of phytochlorin *e* and phytorhodin *g* predicted, namely, that the compounds of Series *b* are derived from the compounds *a*, and probably in such a manner that two atoms of hydrogen are replaced by an atom of oxygen. This substitution, corresponding to the formulas: chlorophyll *a* $C_{55}H_{72}O_6N_4Mg$, *i. e.*, $[C_{82}H_{30}ON_4Mg](CO_2CH_3)(CO_2C_{20}H_{39})$ and chlorophyll *b* $C_{55}H_{70}O_6N_4Mg$, *i. e.*, $[C_{82}H_{28}O_2N_4Mg](CO_2CH_3)(CO_2C_{20}H_{39})$ means a difference of a molecule of oxygen.

Such a result does not appear certain, considering the size of the chlorophyll molecule. The difference, as far as the analyses show, could be CO_2

¹ R. Willstätter and M. Isler, *Ann.*, **390**, 269, 327 (1912); R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," Chap. VI.

² "Ueber die Absorptionsspektren der Komponenten und ersten Derivate des Chlorophylls," R. Willstätter, A. Stoll and M. Utzinger, *Ann.*, **385**, 156 (1911); R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," Chap. XXV.

instead of O_2 and that would be important for the explanation of the chemical function of chlorophyll. The assumed relation between the two components, however, is made more likely by the behavior of the derivatives of chlorophyll *b* toward the Grignard reagent,¹ by which they are converted into components of Series *a*, and further through the course of the decomposition which, in the *b* series, leads to the same aetiophyllin and aetioporphylin.²

The Carotinoids.

In the preparation of the leaf-green, the separation from the yellow accompanying substances, which are extraordinarily widely spread in the plants and are associated with chlorophyll in the chloroplasts, was an important problem. The common occurrence of the yellow dyestuffs with the green, points to a significant physiological role of these carotinoids. In every green leaf, there occur two well-crystallizing nitrogen-free pigments of many common properties, but differing in their behavior towards solvents. One of these, as A. Arnaud³ has made probable, is identical with the carotin of carrots which has been known a long time. The analyses of Willstätter and Mieg⁴ have shown that it is an unsaturated hydrocarbon of the formula $C_{40}H_{56}$. Its companion, xanthophyll,⁵ was yet unknown in substance, in spite of the fact that it predominates in regard to quantity in the leaves. According to its composition, $C_{40}H_{56}O_2$, and its properties, it is to be considered as an oxide of carotin. The hydrocarbon is considerably soluble in petroleum ether, the oxygen compound, on the other hand, only in alcohol. A great affinity for oxygen, which they greedily absorb, particularly in their solutions, is peculiar to both the yellow pigments.

A third carotinoid, the fucoxanthin, is found in the olive-colored seaweeds and it has been recently isolated in pure crystals;⁶ its composition is $C_{40}H_{64}O_6$. It is similar to carotin and xanthophyll in a chemical respect, but distinguished from them by the considerable basic property of its oxygen atoms, bound in the manner of an ether. It forms a characteristic blue hydrochloride which is to be considered as an oxonium salt. The constitution of these yellow pigments has not been explained hitherto, as their decomposition produced only amorphous substances.

Comparative Investigation of the Leaf Pigments.

The description and analysis of chlorophyll and its yellow companions furnish the conditions for the determination of the quantitative relation

¹ R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," p. 331.

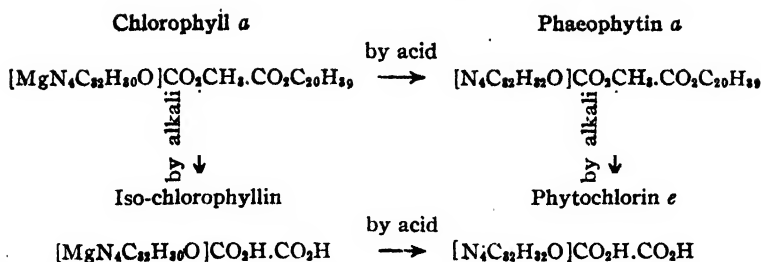
² R. Willstätter and M. Fischer, *Ann.*, **400**, 182 (1913).

³ *Compt. rend.*, **100**, 751 (1885); **102**, 1119 and 1319 (1886); **104**, 1293 (1887); **109**, 911 (1889); *Bull. soc. chim.*, **48**, 64 (1887).

⁴ *Ann.*, **355**, 1 (1907).

⁵ R. Willstätter and W. Mieg, *Ibid.*, **355**, 1 (1907).

⁶ R. Willstätter and H. J. Page, *Ibid.*, **404**, 237, 253 (1914).



The relation between chlorophyll and the chlorophyllin-salts is not a simple one. Two alkali salts, obtained in a homogeneous form, result from each chlorophyll component, according to the conditions of the hydrolysis. One fluoresces, like chlorophyll itself, while the other is lacking fluorescence (chlorophyllin and isochlorophyllin¹). The reaction consists not only in the saponification of two ester groups but, first and foremost, in a specific transformation which is recognized by the appearance of the so-called brown phase. Only a correct explanation of this brown phase² can give the key for the theory of the first steps of decomposition and of the changes which chlorophyll so easily and spontaneously undergoes in its solutions. Let us picture in our minds that, by the action of alkalies on chlorophyll and chlorophyllids, the green color at first changes to an intense brown, to a yellowish brown with the component *a*, to a red with *b*, and then in some minutes, the original chlorophyll color returns in the alkaline medium. The reaction has the appearance of a complete decomposition and a new formation of chlorophyll. Of course, it must be understood that a group, essentially responsible for the chromophoric complex, is changed by hydrolysis and that a new similar one is formed in its place.

We attempt to explain this behavior of chlorophyll as a "re-lactamization," as the opening of an existing lactam ring and the closing of a new ring, similar, but nevertheless stable in alkali. The formation of a new lactam ring can result in several ways: the different series of chlorophyllins and the hardly avoidable occurrence of the weak basic phytochlorins and phytorhodins are explained by it.

The original group may be marked:

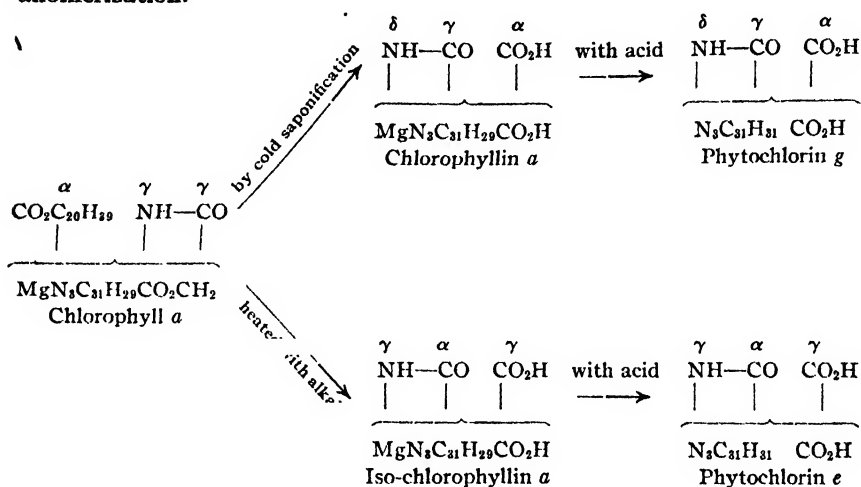


It can so relactamize that, for example, the carboxyl γ enters into combination with another nitrogen group, called δ , or the relactamization can re-

¹ R. Willstätter and M. Utzinger, *Ann.*, 382, 129, 157 (1911); R. Willstätter, M. Fischer and L. Forsén, *Ibid.*, 400, 147 (1913); R. Willstätter and A. Stoll, "Untersuchungen über Chlorophyll," Chap. XVIII.

² R. Willstätter and M. Utzinger, *Ann.*, 382, 128, 135, 139 (1911); R. Willstätter and A. Stoll, *Ibid.*, 387, 317, 326 (1911).

sult in such a manner that another carboxyl, namely, α , unites, for example, with the amino group. This reaction takes place in a different manner when carried out in the cold or with very concentrated alkali at a higher temperature. Chlorophyll also, by standing in alcoholic solution, changes for the same reason. This change, which can be induced by traces of an acid, has been called allomerization.¹



Since the ring-groups, newly formed by the first attack of the alkali on chlorophyll, are more stable than the original ones, the different course of the relectamization causes remaining differences in the products of further decomposition. Corresponding series of simpler composed phyllins and porphyrins therefore originate from the two fundamental derivatives of each chlorophyll component, the chlorophyllin and the isochlorophyllin. There are altogether four series of acids² produced by the alkaline decomposition which lead finally to a single end-product.

From isochlorophyllin *a* arise the dicarboxylic acid cyanophyllin, blue in solution; the dicarboxylic acid erythrophyllin, red in solution; the monocarboxylic acid phyllophyllin, blue, tinged red in solution.

From chlorophyllin *a* result the dicarboxylic acid glaukophyllin, blue in solution; the dicarboxylic acid rhodophyllin, bluish red in solution; the monocarboxylic acid pyrrophyllin, blue, tinged red in solution.

Willstätter and Fischer³ have recently succeeded in splitting off the last carboxyl group from the phyllins and porphyrins by heating them in very small quantities with soda lime. As a result the same aetiophyllin ($\text{C}_{31}\text{H}_{34}\text{N}_4\text{Mg}$) and aetioporphyrin ($\text{C}_{31}\text{H}_{36}\text{N}_4$) have been obtained from

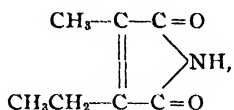
¹ R. Willstätter and A. Stoll, *Ann.*, 387, 357 (1911).

² R. Willstätter, M. Fischer and L. Forsén, *Ibid.*, 400, 147 (1913).

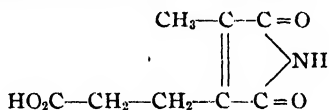
³ *Ann.*, 400, 182 (1913).

the derivatives of chlorophyll *a* and *b*. These nuclei substances are well-crystallizing compounds, which fit into the group picture of the phyllins and the porphyrins previously investigated.

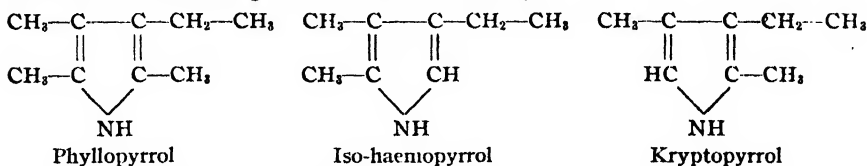
In order to simplify the consideration of the structure of chlorophyll, I would like to restrict myself to a discussion of the formula of aetioporphyrin. It must take into account the results of the oxidation and the reduction of chlorophyll derivatives. By oxidation,¹ phylloporphyrin furnishes compounds which are well known from the investigation of W. Küster² on the decomposition of Haemin. I refer to methyl-ethyl-maleic-imid,



of which more than one molecule is obtained and further to haematic acid, which is produced in molecular quantity:



The reduction³ of the porphyrins yields haemopyrrol, which was chiefly known as a reduction product of the blood dyestuff. M. Nencki and L. Marchlewski⁴ have been the first to obtain it from a chlorophyll derivative. Together with Asahina, I have shown that it has a surprisingly complicated composition, being a mixture of three components, at least. We have isolated from it a tetra-substituted pyrrol, the phyllopyrrol. Hans Fischer and Bartholomaeus,⁵ further O. Piloty⁶ and L. Knorr,⁷ have contributed to the explanation of different haemopyrrol components of which the following are now known exactly:



¹ R. Willstätter and Y. Asahina, *Ann.*, 373, 227 (1910).

² *Z. physiol. Chem.*, 28, 1 (1899); 29, 185 (1900); 44, 391 (1905); 54, 501 (1908); 61, 164 (1909); *Ann.*, 315, 174 (1900).

³ R. Willstätter and Y. Asahina, *Ann.*, 385, 188 (1911).

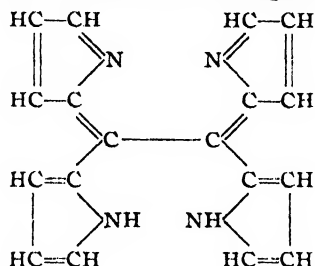
⁴ *Ber.*, 34, 1687 (1901).

⁵ *Ibid.*, 44, 3313 (1911); 45, 1979 (1902); 45, 466 (1912); *Z. physiol. Chem.*, 77, 185 (1912); 80, 6 (1912).

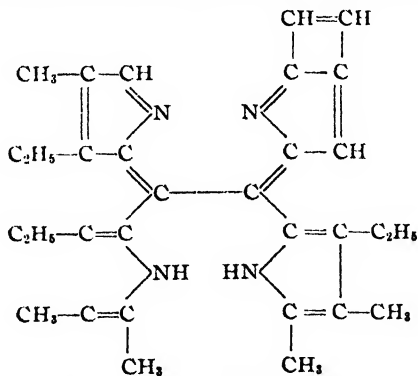
⁶ *Ann.*, 366, 237 (1909); 377, 314 (1910); O. Piloty and E. Quitmann, *Ber.*, 42, 4693 (1909); O. Piloty and J. Stock, *Ann.*, 392, 215 (1912) and *Ber.*, 46, 1008; O. Piloty and K. Wilke, *Ibid.*, 46, 1597 (1913).

⁷ L. Knorr and K. Hess, *Ibid.*, 44, 2758 (1911); 45, 2626 (1912).

The aetioporphyrin therefore is composed of four pyrrol nuclei. The number of its hydrogen atoms is strikingly low, which implies that the pyrrols must be so united and substituted by double bonds or further closing of rings that eight atoms of hydrogens less are required than if there were simple bonds. If the ethyl groups, necessary for the explanation of the oxidation products, are taken into consideration, it does not appear possible to formulate the aetioporphyrin without the assumption of a carbon ring. Several suggestions are met with in the literature on haemin by W. Küster¹ and O. Piloty² as to the combination of the pyrrol nuclei, but the question has not been solved by them. I consider the following formula probable to represent a simple union to a dyestuff of four pyrrol nuclei, of which two are salt-forming and two complex-forming:



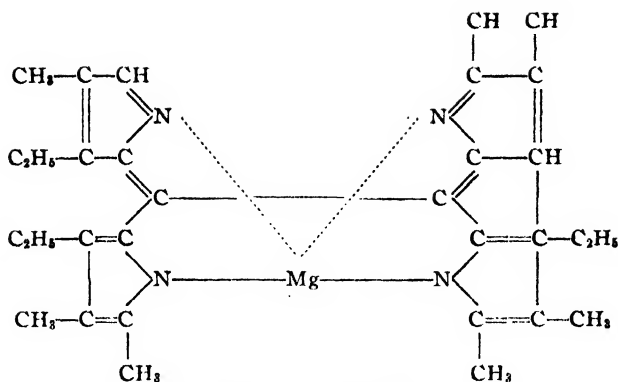
If we substitute this parent substance, in respect of the oxidation products, with three methyl and three ethyl groups and, in respect of the reduction products, with at least another methyl group, there remains finally only so much hydrogen left for the last three carbon atoms that either two double bonds or two carbon rings or one of both must be assumed. If the assumption of a cyclopentane or hexane ring, corresponding to the course of the reduction, is avoided, we arrive, with some probability, at the following formulae for aetioporphyrin and aetiophyllin:



Aetioporphyrin, $C_{41}H_{38}N_4$

¹ *Z. physiol. Chem.*, **82**, 463 (1912).

² *Ann.*, **388**, 313 (1912); **392**, 215 (1912).

Aetiophyllin, $C_{31}H_{34}N_4Mg$.

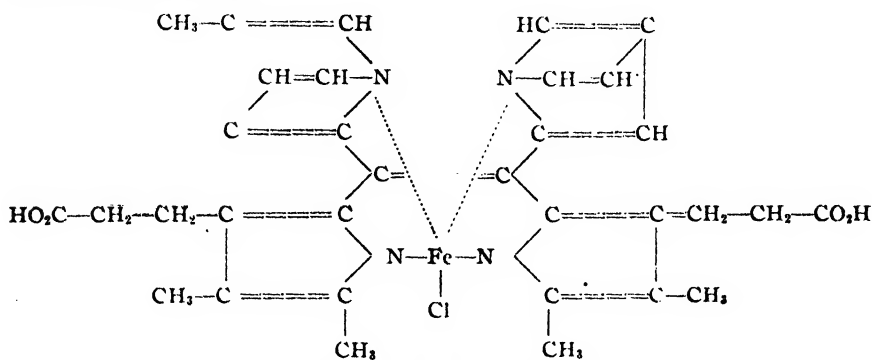
Several details of this formula, as the position of two methyl groups, are arbitrary. The cyclobutene ring could also be attached to the pyrrol in the β, β -position.

The question of the constitution seems to be the more important, as I have succeeded together with M. Fischer,¹ a short time ago, in breaking down the blood dyestuff to aetioporphyrin. There has been obtained, for the first time, a transformation product, from haemin and chlorophyll, whose molecule still stands in close relation to the dyestuff itself. Up to this time, only the decomposition products of haemin and chlorophyll, simple pyrrol derivatives, produced by oxidation and reduction, have been identical. The porphyrins from both pigments exhibited great similarity, which Hoppe-Seyler as well as Schunck and Marchlewski recognized, but nevertheless show considerable differences, for example, in their basic properties.

The porphyrins result from haemin through an entirely different reaction than from chlorophyll, and indeed not simply by the withdrawing of the metal. Haematoporphyrin, the product of the action of hydrobromic acid on haemin, is a dihydroxy acid. It has been possible to reduce haematoporphyrin to a new porphyrin, which I have called haemoporphyrin, by heating with methyl alcoholic potassium hydroxide and pyridine. This product differs in its composition from haematoporphyrin by minus two hydroxyl groups. Like the rhodoporphyrin, with which it is isomeric, it can be decarboxylated by heating with soda lime. From the composition $C_{31}H_{36}N_4$ of the aetioporphyrin so obtained, it follows that haemoporphyrin corresponds to the formula $C_{33}H_{38}O_4N_4$, and consequently haemin does not correspond to the generally adopted formula $C_{34}H_{32}O_4N_4 \cdot FeCl$ but to the formula $C_{33}H_{32}O_4N_4 \cdot FeCl$. While the aetioporphyrin of the formula $C_{31}H_{36}N_4$ already appears strikingly poor in hydrogen, haemin, $C_{33}H_{32}O_4N_4 \cdot FeCl$, is derived from a parent substance, $C_{31}H_{34}N_4$, still poorer

¹ *Z. physiol. Chem.*, 87, 423 (1913).

by two hydrogen atoms, which renders it necessary to assume double bonds as well as peculiar carbon rings. Upon the basis of a new research¹ on the reactions leading from haemin to haematoporphyrin, I have tried to develop a constitutional formula of haemin explaining the behavior upon oxidation and reduction and also the porphyrin formation. In many details it has not been proved but, as I hope, it may serve to guide further investigation.



Haemin, C₃₃H₃₂O₄N₄FeCl.

Although chlorophyll and haemin have been traced back to the same aetioporphyrin, which can be called a parent substance, we do not draw the conclusion of a near constitutional relationship between chlorophyll and haemin from the investigations of the decomposition. In one, there is magnesium, in the other iron, in one, ester formation with phytol, in the other a combination with globin. In addition to such differences, corresponding to the function of a different kind, there are further significant dissimilarities in the real nucleus of the dyestuff which have disappeared only by far-reaching decomposition. On the way from haemin to aetioporphyrin there are two transformations, which essentially change the construction of the molecule, namely, the transition from haemin to haematoporphyrin and from this to haemoporphyrin, which is isomeric with the porphyrins of chlorophyll. Between chlorophyll and aetiophyllin and even between chlorophyll and the first dibasic porphyrins, as cyanoporphyrin or erythroporphyrin, there are two steps, essentially transforming the molecule. They cannot be compared with the reactions of haemin.

Future investigations on the constitution of chlorophyll will still find important problems. The relations between the two chlorophyll components and the transformations which lead from chlorophyll to the chlorophyllins and from the chlorophyllins to the dibasic phyllins, are to be explained and the structure of aetioporphyrin is still to be investigated in important details. Of still greater importance are the questions which

¹ R. Willstätter and M. Fischer, *Z. physiol. Chem.*, **87**, 423 (1913).

plant physiology asks and their solution will perhaps be aided by the isolation and the study of the components of the leaf dyestuff. These questions refer to the possibility of a chemical function of chlorophyll and to its nature.

BERLIN-DAHLEM, GERMANY.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

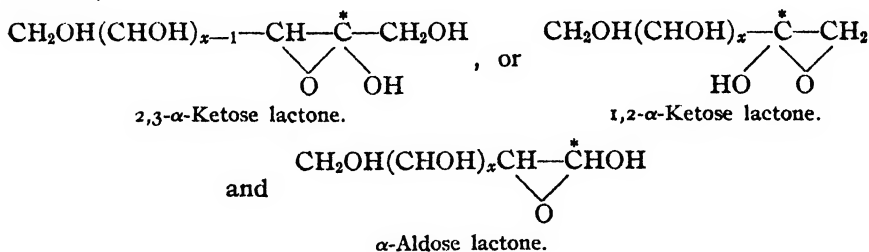
**ON THE ESTERS, AS WELL AS THE MONOMOLECULAR β - AND γ -LACTONES, OF *D*-MANNONIC AND *D*-GLUCONIC ACIDS;
ON ORTHO-BIS-*D*-GALACTONIC ACID, *D*-GALACTONIC
 γ -LACTONE AND ITS MONO-HYDRATE.**

BY OSCAR F. HEDENBURG.

Received December 5, 1914.

A very condensed description of the properties and methods of preparation of the various compounds named in the above title has very recently been published by Nef,¹ who also discusses in detail the significance of the discovery of α -, β - and γ -lactones of the polyhydroxy acids, $C_nH_{2n}O_{n+1}$, in coming to a decision on the question of the constitution of the α - and β -modifications of aldose and ketose sugars, as well as of the α - and β -glucosides. He has reached the conclusion that the various crystalline forms of the simple sugars,² including also malt and milk sugars, are to be represented either by the free ketose or aldose structure,

$\begin{array}{c} O \\ || \\ CH_2OH(CHOH)_x - C - CH_2OH \end{array}$ and $CH_2OH(CHOH)_{x+1} - CHO$ (or
at times by a corresponding ketose or aldose monohydrate structure,
analogous to chloral hydrate, etc.), or, by a monomolecular α -lactone
formula,



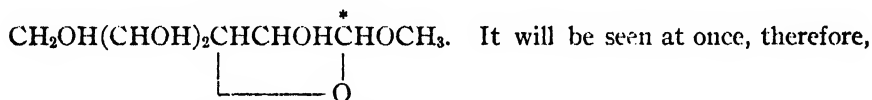
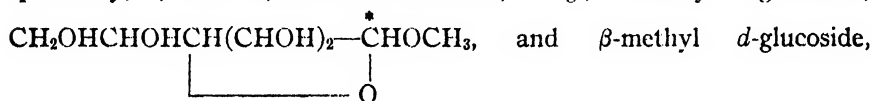
Generally only one of these two, or, in the case of the ketoses, three forms,

¹ *Ann.*, **403**, 273-9, 306-331 (1914).

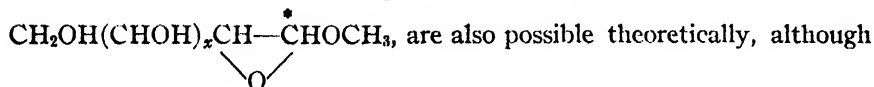
² In many cases the hydrazones, oximes, anilides and osazones of aldose and ketose sugars are known to show mutarotation; this is unquestionably due to the existence of two or more analogous structural isomers, which have frequently been isolated, but have hitherto almost invariably been regarded as space isomers.

can be obtained pure by crystallization; the other modification, when isolated by Tanret's method for example, usually consists only of mixed crystals of which theoretically a limitless number are possible. Thus α -*d*-glucose, $[\alpha]_D^{20} = +104^\circ$, m. p. 156° , must be represented by the α -lactone formula, whereas Tanret's β -*d*-glucose, $[\alpha]_D^{20} = +22.5^\circ$, can not conceivably represent the pure aldehyde modification of *d*-glucose whose specific rotation must be slightly laevo, but consists of a mixture of about 80% of aldehyde sugar, contaminated with 20% of α -lactone. Crystallized *d*-mannose, $[\alpha]_D^{20} = -2^\circ$, on the other hand, corresponds to the free aldehyde form, whereas the α -lactone modification, which exists to the extent of about 20% in an aqueous solution of *d*-mannose after 24 hrs. standing, $[\alpha]_D^{20} = +16^\circ$, and which must undoubtedly possess $[\alpha]_D^{20} =$ over $+100^\circ$, has not as yet been isolated in a pure condition. Crystallized *d*-fructose finally, whose melting point invariably ranges from 105° – 115° , probably consists of a mixture of the two α -lactones, 2,3- and 1,2- α -*d*-fructose, etc., etc.

The so-called α - and β -glucosides, on the other hand, possess respectively, γ - and β -lactone structure, e. g., α -methyl *d*-glucoside,



It will be seen at once, therefore, that only the α -glucosides retain the γ -lactone structure hitherto ascribed in all the text books also to the α - and β -sugar modifications, as well as to the β -glucosides; they should therefore be renamed γ -glucosides in accord with their structure, especially as α -glucosides of the formula,



representatives of this class have not yet actually been isolated.

The problem assigned to me by Dr. Nef, therefore, was to confirm and extend his observations on the preparation and properties of the various derivatives of *d*-mannonic, *d*-gluconic and *d*-galactonic acids named above, as well as to make a thorough search for other derivatives possibly overlooked by him and especially to analyse, titrate and to determine the molecular weights and physical constants of the new compounds obtained. Many of my results are to be found in Nef's paper in Liebig's *Annalen*; they are, however, given here in greater detail and many new observations are included.

Experimental Part.

I. On Ethyl *d*-Mannonate, and on *d*-Mannonic β - and γ -Lactones.

***d*-Mannonic β -Lactone.**—This is the normal and practically the only lactone formed from free *d*-mannonic acid, $[\alpha]_D^{20} = -1^\circ$,¹ at ordinary temperatures; γ -lactone formation also takes place, although very slowly at lower temperatures, but far more rapidly as the temperature is raised. In order, therefore, to obtain the maximum yield of β -lactone an aqueous solution of *d*-mannonic acid should not be heated higher, nor longer, than absolutely necessary. Such a solution² is best prepared by adding the calculated amount of crystallized oxalic acid in water to an aqueous solution of calcium *d*-mannonate heated to 50° . The mixture is thereupon cooled within five minutes to about 20° and the calcium oxalate filtered off as rapidly as possible. The water must also be distilled off quickly from the filtrate at the lowest possible temperature and pressure. The residual gum may then be transformed into the β -lactone by prolonged heating under 20 mm. pressure at first at 50° , but finally up to 100° .

The β -lactone, which was used to determine constants and to perform various experiments (see below), was prepared from free *d*-mannonic acid obtained from barium *d*-mannonate by rapid treatment with dilute sulfuric acid at 95° to 98° . The salt was prepared by dissolving *d*-mannonic γ -lactone in a dilute solution of one and one-half times the calculated amount of crystallized barium hydroxide and heating for ten minutes on a boiling water bath. The calculated amount of sulfuric acid was then added to liberate mannonic acid; the solution was thereupon rapidly adjusted so that it contained only a trace of barium, filtered free from barium sulfate, cooled and distilled at 20 mm. pressure with the surrounding bath at 40 – 45° until no more moisture condensed in the neck of the flask. The resulting gum, a mixture of *d*-mannonic acid and β - and γ -lactones, is very soluble in absolute alcohol. Eight grams of γ -lactone were changed into barium *d*-mannonate by 21.28 g. barium hydroxide. The gum, obtained as described above, was kept in the flask about 15 hrs. longer and became partly crystalline. The gum that still remained dissolved readily, but the crystalline mass went into solution with considerable difficulty in 400 cc. of boiling absolute alcohol. After distilling off half of the solvent at ordinary pressure and cooling, 1.45 g. of pure β -lactone, melting at 161 – 162° , $[\alpha]_D^{20} = +111.85^\circ$, came out in transparent, octahedral crystals. Mixed crystals of β - and γ -lactones, 3.66 g., melting from 134 – 150° , were obtained in four subsequent fractions on further concentration of the alcoholic filtrate.

Another experiment was carried out with 11 g. of γ -lactone in the same way, but here the adjustment for barium was made in one-half an hour,

¹ *Ann.*, 403, 314 (1914).

² *Ibid.*, 403, 310 (1914).

i. e., more quickly than in the former experiment. The residual gum, after standing about 36 hrs. also became partly crystalline, and solution was effected with difficulty by 500 cc. of boiling absolute alcohol. After filtering off traces of barium salt, the solution was concentrated to about 300 cc. by distillation at 20 mm. pressure, and in the course of two days 4.48 g. of β -lactone, melting between 156° and 162° , separated out without seeding. The filtrate was concentrated to about 100 cc. and 1 g. of impure γ -lactone was obtained, which, recrystallized from 100 cc. of absolute alcohol, gave 0.65 g. melting at 149.5° with $[\alpha]_D^{20} = +57.05^\circ$.

The following analytical results, molecular weight determination, specific rotation and other data were obtained with a preparation of pure β -lactone melting, after a second crystallization from absolute alcohol, between 161° and 162° . The β -lactone requires about 100 parts of boiling absolute alcohol for solution, from which, on standing at room temperatures, a very large amount crystallizes out unchanged in transparent, measurable octahedra. This lactone can be recrystallized from water, but this is not an advantageous process since an aqueous solution changes rapidly, even at 20° , to free *d*-mannonic acid.

0.2083 g. gave 0.3096 g. CO_2 and 0.1072 g. H_2O .

Calc. for $\text{C}_6\text{H}_{10}\text{O}_4$: C, 40.45; H, 5.62; found: C, 40.53; H, 5.72.

A titration was carried out as follows: the lactone was dissolved in an excess of 0.1 *N* KOH and the solution heated on a boiling water bath for 10 min. to form completely the potassium salt. The cooled solution was titrated back with 0.1 *N* H_2SO_4 (phenolphthalein as indicator) to excess, whereupon carbon dioxide was expelled by boiling. The solution, cooled again, was adjusted to the end point with 0.1 *N* KOH. 0.5051 g. used 28.26 cc. 0.1 *N* KOH instead of 28.36 cc. calculated for $\text{C}_6\text{H}_{10}\text{O}_4$.

A molecular weight determination was carried out according to the boiling point method of McCoy¹ with 0.3552 g. substance in freshly prepared absolute alcohol.²

| Vol. of solution. Cc. | Rise in B. P. | Mol. wt. found. | Mol. wt. calc. for $\text{C}_6\text{H}_{10}\text{O}_4$. |
|--------------------------|------------------|--------------------|---|
| 25.60 | 0.107° | 202.0 | |
| 28.50 | 0.102° | 190.6 | |
| 33.30 | 0.096° | 173.3 | 178 |

Av., 185.3

The specific rotation of the β -lactone in 4% solution was found to be $+111.85^\circ$ six minutes after solution, for 0.4021 g. dissolved in 10.0456 g. of water gave $+4.35^\circ$ in a one decimeter tube. The specific gravity of the solution was considered 1.011, as were all subsequent 4% aqueous solutions. Observations were made with this tube kept at room temperature for 23 days to follow the changes in optical activity.

¹ *Am. Chem. J.*, 23, 353 (1900).

² The absolute alcohol used here and later was freshly prepared by redistillation over quick-lime. A middle fraction was used after standardization by determination of the molecular weight of benzoic acid.

TABLE I.

| Time after solution. | Observed angle. | $[\alpha]_D$. |
|----------------------|-----------------|----------------|
| 6 min. | +4.35° | +111.85° |
| 1 hr. 40 min. | +3.95° | +101.54° |
| 3 hr. 40 min. | +3.30° | + 84.84° |
| 5 hr. 30 min. | +2.53° | + 65.03° |
| 20 hr. | +1.18° | + 30.28° |
| 1 day 2 hr. | +1.15° | + 29.57° |
| 1 day 4 hr. 30 min. | +1.10° | + 28.28° |
| 1 day 20 hr. | +1.10° | + 28.28° |
| 2 days 2 hr. | +1.10° | + 28.28° |
| 2 days 21 hr. | +1.10° | + 28.28° |
| 3 days 4 hr. | +1.10° | + 28.28° |
| 4 days 20 hr. | +1.00° | + 25.71° |
| 5 days 21 hr. | +1.00° | + 25.71° |
| 6 days 20 hr. | +1.05° | + 27.00° |
| 15 days | +1.20° | + 30.85° |
| 23 days | +1.55° | + 39.85° |

When the specific rotation reached +28.28°, the solution evidently contained in equilibrium about 25% of β -lactone together with about 75% of free *D*-mannonic acid. Traces of γ -lactone were also present. At this point 70% of the original β -lactone can be recovered, either by evaporation of the aqueous solution over H_2SO_4 *in vacuo* or by rapid distillation at 20 mm. pressure with the bath at 40°. Thus a solution of 8.1 g. of β -lactone in 32.4 g. of water which stood for 24 hrs. was freed from water by distillation at 20 mm. pressure with the surrounding bath at 35–40°. Before all the water was removed crystals separated out; the crystalline residue was loosened and removed from the flask with 100 cc. of cold, absolute alcohol. The crystals thus obtained, 6.58 g., melted between 138° and 155° and gave $[\alpha]_D^{20} = +101.33^\circ$, or, after 29 hrs. standing at ordinary temperatures, +32.18°; this showed that the mixed crystals contained about 90%, 5.9 g., of β -lactone. Furthermore, the alcoholic filtrate gave, after removing the solvent by distillation at 20 mm. pressure, 1.38 g. of solid residue, which yielded, on recrystallization from 25 cc. of warm, absolute alcohol (60°), 0.7 g. of mixed crystals melting between 132° and 142° with $[\alpha]_D^{20} = +77.1^\circ$, and containing, therefore, about 40% of β -lactone (0.28 g.). 6.2 g. or 76.54% of the β -lactone was therefore recovered unchanged.

Judging from the optical activity of an aqueous solution of β -lactone at the end of 23 days (+39.85°), as shown in Table I, about 50% of *D*-mannonic γ -lactone must now have been present, since the specific rotation of pure γ -lactone is +51.8°, whereas equilibrium exists between *D*-mannonic acid and *D*-mannonic β -lactone at +28.28°. The abnormal γ -lactone is, therefore, slowly formed from free *D*-mannonic acid by loss of water, and since this reaction, according to observations on pure γ -lac-

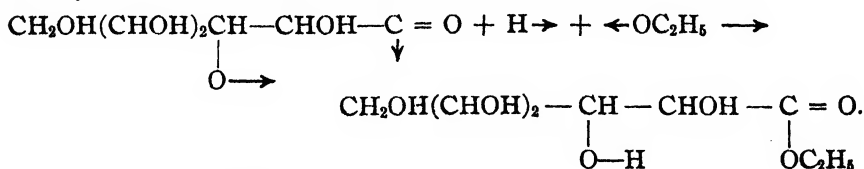
tone, is shown in Table I. The results are as shown in the table.

When solid *d*-mannonic β -lactone is heated to its melting point, γ -lactone formation also results, which must obviously be due to an intermediate formation of *d*-mannonic acid, produced by the presence of unavoidable traces of water. Thus, 0.3 g. β -lactone, heated in a small distilling flask in an oil bath kept at 156° for three-quarters of an hour, was transformed into 0.3 g. hard gum; this gave, when dissolved in 7.07 g. cold water, $\alpha = 1.3^\circ$ in a one decimeter tube, whence $[\alpha]_D^{20} = +63.9^\circ$; after 18 days' standing at 20° , the specific rotation had fallen to $+45.7^\circ$. About 80% of the β -lactone must, therefore, have been transformed into γ -lactone.

The γ -lactone is also formed by loss of alcohol, when ethyl *d*-mannonate is heated for a short time at its melting point (cf. ethyl *d*-mannonate).

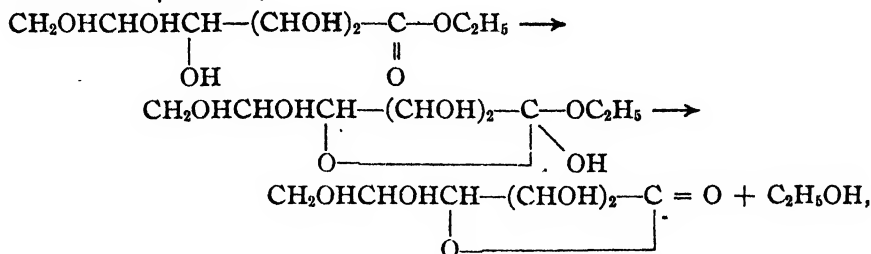
A fairly rapid transformation into γ -lactone also takes place, when an aqueous solution of β -lactone, or of *d*-mannonic acid is heated at 100° . Thus an approximately 4% aqueous solution of *d*-mannonic β -lactone (0.6244 g. in 14.4346 g. H_2O), when heated for one hour on a boiling water bath and cooled quickly with running water, gave at first a specific rotation of $+48.43^\circ$ ($\alpha = +2.03^\circ$ in a 1 dc. tube); this fell, after standing $17\frac{1}{2}$ hrs. at room temperature, to $+37.7^\circ$. In a second experiment, in which an aqueous solution containing 0.6172 g. β -lactone was heated for five hours on a boiling water bath, the specific rotation of the cold solution was found to be $+48.68^\circ$ at 20° (14.1991 g. H_2O ; $\alpha = +2.05^\circ$ in a 1 dc. tube); this changed to $+45.83^\circ$ only, after 18 hrs. standing at room temperature. On evaporating the solution over H_2SO_4 *in vacuo*, crystals, melting between 151° and 152° , and giving $[\alpha]_D^{20} = +52.19^\circ$ (0.5665 g. in 13.2705 g. H_2O gave $\alpha = +2.15^\circ$ in a 1 dc. tube), were obtained; the specific rotation fell to $+49.02^\circ$ after 51 hrs. The crystals were evidently almost pure γ -lactone. This explains why Nef¹ succeeded in obtaining practically pure γ -lactone by simply evaporating, with occasional stirring, an aqueous solution of free *d*-mannonic acid, of *d*-mannonic β -lactone, or of ethyl *d*-mannonate in the presence of a small amount of hydrogen chloride.

Ethyl *d*-Mannonate.—This substance is always formed by the addition of ethyl alcohol to the active molecules of *d*-mannonic β -lactone,



¹ *Ann.*, 403, 309 (1914).

Small amounts of hydrogen chloride or of free *D*-mannonic acid facilitate very much the addition of the reagent. Since, however, the ester is easily converted by intramolecular addition and subsequent loss of alcohol into *D*-mannonic γ -lactone,



a reaction which is also enormously accelerated by the presence of hydrogen chloride or of free *D*-mannonic acid, it is possible to prepare pure ethyl *D*-mannonate only under very definite conditions.

As a result of certain experiments (see below), from which mixed crystals of *D*-mannonic γ -lactone and of ethyl *D*-mannonate were obtained, a method for preparing the ethyl ester quantitatively from the β -lactone was developed as follows: 62 g. of the well-powdered β -lactone were covered in a stoppered flask with 200 cc. of cold absolute alcohol containing 1% of dry hydrogen chloride, and the mixture was thoroughly shaken. Within 25 minutes the compact β -lactone was replaced by a bulky mass of filamentous crystals. The mixture was allowed to stand, however, for 24 hrs., when the crystals were filtered off and thoroughly washed free from hydrogen chloride by cold absolute alcohol. 1.04 g. melting at 158–159° were obtained; on crystallizing a portion of these, 0.53 g., from 60 cc. of hot absolute alcohol, 0.38 g. of the pure, optically inactive product, melting at 160–161°, was recovered. No more ethyl ester could be obtained from the alcoholic filtrates containing hydrogen chloride by removal of the alcohol at reduced pressure, for the solid residue, 1.28 g., now gave, on rinsing with a small amount of absolute alcohol, 0.72 g. of insoluble crystals melting between 148° and 151° with $[\alpha]_D^{20} = +49.21^\circ$. These evidently consisted of almost pure γ -lactone produced from the ester by decomposition by the hydrogen chloride.

A better yield was subsequently obtained by using 2.25 g. of β -lactone and only 100 cc. of cold 1% alcoholic hydrogen chloride; the crude, insoluble product, 2.12 g., melted between 155° and 157° and gave by crystallization from 200 cc. of absolute alcohol 1.49 g. of pure ester melting from 160–161°.

The ethyl ester can moreover only be obtained from *D*-mannonic γ -lactone by its preliminary conversion into free *D*-mannonic acid and β -lactone. The β -lactone then adds alcohol as described above. Thus 2 g. of the γ -lactone were dissolved in one and one-half times the calculated volume

of normal sodium hydroxide solution, 16.86 cc., and the solution was warmed to form the sodium salt. Then, after cooling, an equivalent amount of normal hydrochloric acid was added; the water was distilled off at 20 mm. pressure with the bath at 40°. A gum containing sodium chloride was left, which weighed 3.41 g. and of which 3.04 g. dissolved in 80 cc. of hot absolute alcohol. Concentrated alcoholic hydrogen chloride was added to make the solution contain 1% of hydrogen chloride, and 0.74 g. of ester melting at 160–161° was obtained.

The following analysis, molecular weight determination and the data on the action of water and heat were obtained by the use of a pure preparation of ethyl *d*-mannonate melting at 160–161°:

0.1728 g. gave 0.2709 g. CO₂ and 0.1115 g. H₂O.

Calc. for C₈H₁₆O₇: C, 42.87; H, 7.14; found: C, 42.76; H, 7.17.

The molecular weight was determined with 0.5083 g. substance in boiling absolute alcohol by McCoy's method; the average of three readings (232, 243, 246) was 240 instead of 224 calculated for C₈H₁₆O₇.

Pure ethyl *d*-mannonate, which is very soluble in water, has no optical activity; but the solution becomes faintly dextrorotatory within five hours, due to hydrolysis of the ester, and to the subsequent change of free *d*-mannonic acid into β - and γ -lactones, *e. g.*, 0.4163 g. of substance in 10.0653 g. of water showed no activity in a one decimeter tube, but the Table II records a series of readings which show the changes wrought by the transformation of the ethyl ester.

TABLE II.

| Time after solution. | Observed angle. | $[\alpha]_D$. |
|----------------------|-----------------|----------------|
| 5 hrs. 10 min. | +0.15° | + 3.53° |
| 1 day | +0.22° | + 5.48° |
| 3 days | +0.52° | +12.95° |
| 4 days | +0.62° | +15.44° |
| 5 days | +0.65° | +16.16° |
| 6 days | +0.70° | +17.44° |
| 7 days | +0.75° | +18.68° |
| 8 days | +0.80° | +19.93° |
| 10 days | +0.85° | +21.17° |
| 16 days | +1.08° | +26.90° |
| 26 days | +1.15° | +28.65° |

If the specific rotation at the end of 26 days be calculated on the basis of lactone produced by hydrolysis (0.4163 g. of ester gives 0.3308 g. of lactone), it becomes +35.74°, which is in fair agreement with the optical activity (+39.85°) of a solution of β -lactone, or of free *d*-mannonic acid, at the end of 23 days (see above).

It is evident from the data given, and this was also proved by special experiment, that the ester can be recovered unchanged from an aqueous solution, if the water be removed within an hour; thus, 0.3711 g. of ester

in 8.9664 g. H_2O showed no optical activity; the solvent was distilled off at once at 20 mm. pressure with the bath at 40° . The residue was crystallized from 10 cc. of absolute alcohol and 0.24 g. of ester, melting at $160\text{--}161^\circ$, was recovered.

The ester is rapidly converted into γ -lactone by loss of ethyl alcohol, perhaps with intermediate formation of β -lactone (see above) when heated in a distilling flask under reduced pressure just above its melting point. One gram of ester, heated between 162° and 170° for about one-half an hour, lost 0.24 g. in weight. The stiff residual gum, 0.76 g. recrystallized from about 10 cc. of absolute alcohol, gave 0.37 g. *D*-mannonic γ -lactone which melted between 150° and 154° with $[\alpha]_D^{20} = +51.52^\circ$. A second experiment with 1.2 g. ester, which was heated at 164° for 50 mins., gave 0.93 g. hard gum from which 0.63 g. *D*-mannonic γ -lactone, melting at $151\text{--}152^\circ$ and with $[\alpha]_D^{20} = +48.25^\circ$ was obtained.

Ethyl *D*-mannonate, which is optically inactive, and *D*-mannonic γ -lactone ($[\alpha]_D^{20} = +51.8^\circ$) give a large number of mixed crystals melting from $135\text{--}155^\circ$, the specific rotations of which naturally fall between those of the pure substances and remain constant for some hours. For a long time Nef and I thought that a third monomolecular lactone of *D*-mannonic acid was present in these mixtures, but they all gave an iodoform test due to the presence of ethyl *D*-mannonate.

Thus, a solution of 0.5 g. of β -lactone in 100 cc. of absolute alcohol containing a small amount of dry hydrogen chloride was heated at about 75° under a reversed condenser for two hours. The alcohol was distilled off at 20 mm. pressure with the temperature of the surrounding bath between 30° and 35° ; the residue was then crystallized from 30 cc. of absolute alcohol. The needles obtained, 0.2 g., melted at 139° , and gave $[\alpha]_D^{20} = +35.88^\circ$ without change after 24 hrs. standing.

Again, 1 g. of β -lactone and 30 cc. of absolute alcohol, heated in a sealed tube at 120° for 5 hrs., gave 0.83 g. of concentric needles, melting between 140° and 142° with $[\alpha]_D^{20} = +45.63^\circ$; the product was, therefore, mainly *D*-mannonic γ -lactone mixed with about 10% of ethyl ester.

A preparation consisting of mixed crystals of *D*-mannonic β - and γ -lactones (the melting point and specific rotation of which had not been determined) when treated with cold absolute alcohol containing a small amount of dry hydrogen chloride, soon deposited bulky, apparently homogeneous crystals melting at $140\text{--}141^\circ$, the specific rotation of which remained constant in aqueous solution at $+24.8^\circ$.

Nef¹ and Lewis obtained many such mixed crystals when working with mixtures of *D*-mannonic acid and *D*-mannonic β - and γ -lactones both in the presence and absence of hydrogen chloride.

Finally it should be especially emphasized that pure *D*-mannonic γ -lac-

¹ *Ann.*, 403, 310 (1914).

tone, [formed in the colorless solution] chloride, gives no ethyl ester.

***d*-Mannonic γ -Lactone.**—This lactone was discovered by Fischer and Hirschberger,¹ but it was contaminated with β -lactone so that it melted over a range, 149–153°, and showed a high specific rotation, +53.81°, in 10% concentration. Nef² has shown that the pure γ -lactone melts sharply at 151° and gives $[\alpha]_D^{20} = +51.8^\circ$ in 4% concentration; this lactone moreover remains unchanged in aqueous solution at 20° for a long time, whereas the far more strongly active β -lactone, $[\alpha]_D^{20} = +111.85^\circ$, is rapidly hydrolyzed to mannonic acid (a gum very soluble in cold absolute alcohol, $[\alpha]_D^{20} = -1^\circ$) to the extent of 75%, at which point the β -lactone exists in equilibrium at 20° with the free acid. Since the γ -lactone has repeatedly been analyzed and titrated, it was only necessary to make a molecular weight determination and thus prove that the substance is monomolecular. The determination was made with McCoy's boiling point apparatus, using absolute alcohol as the solvent, in which it is far more soluble than the β -lactone.

0.5391 g. of lactone gave 199 for the molecular weight instead of 178 calculated for $C_6H_{10}O_6$.

| | | | | | | Av. |
|---------------------|--------|--------|--------|--------|--------|-----|
| Vol. of solution. | 28.60 | 30.00 | 31.20 | 33.20 | 35.50 | |
| Rise in B. P. . . . | 0.145° | 0.141° | 0.134° | 0.130° | 0.119° | |
| Mol. wt. found. | 203 | 198 | 201 | 194 | 199 | 199 |

The γ -lactone reacts with water when heated in aqueous solution at 100°. *d*-Mannonic acid is first formed, from which the β -lactone is then produced; its presence can easily be proved since the specific rotation of the solution decreases in a few hours. The following experiments illustrate these changes: An approximately 4% solution of γ -lactone (0.5480 g. in 13.5908 g. H_2O), when heated for one hour on a boiling water bath and cooled quickly with running water, gave at first a specific rotation of +50.53° ($\alpha = +1.98^\circ$ in a 1 dc. tube); this became +48.5° after 72 hrs. standing at room temperatures. Another experiment, in which an aqueous solution of γ -lactone was heated for five hours on a boiling water bath, gave on rapid cooling a specific rotation of +51.22° (0.5311 g. in 13.0843 g. H_2O gave $\alpha = +2.02^\circ$ in a 1 dc. tube); this fell after 15 hrs. to +46.91°. The solution, evaporated over H_2SO_4 *in vacuo*, yielded a solid residue, 0.5374 g, melting between 132° and 148°; 0.4933 g. of this dissolved in 10.5960 g. H_2O gave a specific rotation of +59.14° ($\alpha = +2.66^\circ$ in a 1 dc. tube); after 40 hrs. standing this had fallen to +46.69°. Evidently more β -lactone was formed from free *d*-mannonic acid, also at first present, which accounts for the higher specific rotation of the solid residue.

¹ *Ber.*, 22, 3231 (1889).

² *Ann.*, 403, 316 (1914).

II. On Ethyl *d*-Gluconate and on *d*-Gluconic β - and γ -Lactones.

Nef presents with great precision in his *Annalen* paper¹—the end result of years of experimental work—the most favorable conditions, A, for the conversion of free *d*-gluconic acid (a viscous syrup, $[\alpha]_D^{20} = -1.7^\circ$, very soluble in cold absolute alcohol), or of *d*-gluconic β -lactone into ethyl *d*-gluconate (bulky, fibrous crystals, $[\alpha]_D^{20} = -1^\circ$, melting between 60° and 65°); B, for the transformation of free *d*-gluconic acid or of ethyl *d*-gluconate into normal *d*-gluconic β -lactone (transparent prisms, $[\alpha]_D^{20} = +61.7^\circ$, melting point 152° , and soluble in 100 parts of boiling absolute alcohol); and finally, C, for the conversion of any of these three substances at higher temperatures into the abnormal and more stable *d*-gluconic γ -lactone (heavy needles, melting from 134 – 136° , $[\alpha]_D^{20} = +67.8^\circ$, and soluble in 14 parts of hot absolute alcohol). The situation in this series is complicated by the fact that here alone, among all the polyhydroxy acids $C_nH_{2n}O_{n+1}$ as yet studied, a very marked tendency to polymolecular anhydride formation is noticeable. This phenomenon is due, as Nef has shown, to an intermediate formation of *nascent* monomolecular *d*-gluconic α -lactone,² $CH_2OH(CHOH)_3CH-C=O$.



The study of these polygluconic anhydrides, which are precipitated from aqueous solution by alcohol, is at present being continued in this laboratory and has been found to present great experimental difficulties; I have consequently limited myself mainly to a further study of the physical and chemical properties of ethyl *d*-gluconate, and of the monomolecular β - and γ -lactones of *d*-gluconic acid.

***d*-Gluconic β -Lactone.**—The new, normal β -lactone has been obtained both from free *d*-gluconic acid and from ethyl *d*-gluconate (see this).

Nef² has given precise directions whereby a yield of about 20% of β -lactone can be obtained from anhydrous calcium *d*-gluconate.

I prepared *d*-gluconic β -lactone from free *d*-gluconic acid by treatment of a warm (60°), aqueous solution of 10 g. of anhydrous calcium *d*-gluconate with 2.93 g. of crystallized oxalic acid in water. The solution of *d*-gluconic acid, cooled at once to 20° and filtered, was freed from water by distillation at 20 mm. pressure with the surrounding bath at 40° , until a syrup, containing about 10 g. of water, resulted, whereupon 100 cc. absolute alcohol were added to precipitate traces of calcium salt as well as polygluconic anhydrides. The residual gum, 8.18 g., obtained from the filtrate by removal of water and alcohol at reduced pressure, yielded, on dissolving in about 10 cc. warm absolute alcohol, 1.04 g. β -lactone (in two fractions) melting from 151 – 154° ; this, recrystallized from 25 cc.

¹ *Ann.*, 403, 322–331 (1914).

² *Ibid.*, 403, 322 (1914).

³ *Ibid.*, 403, 323–325 (1914).

absolute alcohol, gave 0.75 g. pure β -lactone melting
63.4° five minutes after solution.

th $[\alpha]_D^{20} =$

The following constants and analyses were obtained with comparisons
of pure β -lactone:

0.1237 g. gave 0.1855 g. CO_2 and 0.0566 g. H_2O .

Calc. for $\text{C}_6\text{H}_{10}\text{O}_4$: C, 40.45; H, 5.92; found: C, 40.90; H, 5.13.

The titration was carried out as previously described. 0.4227 g. substance used
23.61 cc. 0.1 *N* KOH instead of 23.75 cc. calculated for $\text{C}_6\text{H}_{10}\text{O}_4$.

The molecular weight of β -lactone, determined by the boiling point method in
McCoy's apparatus (see *d*-mannonic β -lactone) using absolute alcohol and 0.4801 g.
substance, was found to be 199.3 instead of 178 calculated for $\text{C}_6\text{H}_{10}\text{O}_4$.

Av.

| | | | | | |
|-----------|-----------|-----------|-----------|-----------|-----------|
| 0.1237 g. | 0.1855 g. | 0.0566 g. | 23.61 cc. | 0.4227 g. | 23.75 cc. |
| | | | | | 108° |
| | | | | | 199.3 |

Nef¹ found the specific rotation of *d*-gluconic β -lactone at 20° to be
+61.7° twelve minutes after solution. The specific rotation was found
by me to be +63.4° five minutes after solution (0.4288 g. dissolved in
9.4233 g. H_2O at 20° gave $\alpha = +2.79^\circ$ in a 1 dc. tube). The changes
in optical activity of this solution for nearly eight days (after which
constancy ensued) are recorded in Table III.

TABLE III.

| Time after solution. | Observed angle. | $[\alpha]_D$. | Time after solution. | Observed angle. | $[\alpha]_D$. |
|-------------------------|--------------------|----------------|-------------------------|--------------------|----------------|
| 5 min. | +2.79° | +63.40° | 46 min. | +1.64° | +37.25° |
| 7 min. | +2.75° | +62.50° | 59 min. | +1.27° | +29.13° |
| 10 min. | +2.70° | +61.35° | 1 hr. 16 min. | +0.98° | +22.37° |
| 12 min. | +2.67° | +60.60° | 1 hr. 30 min. | +0.76° | +17.27° |
| 14 min. | +2.60° | +60.47° | 1 hr. 45 min. | +0.67° | +15.23° |
| 17 min. | +2.54° | +59.05° | 2 hr. 20 min. | +0.50° | +11.36° |
| 18½ min. | +2.50° | +58.13° | 2 hr. 35 min. | +0.45° | +10.21° |
| 19 min. | +2.47° | +57.44° | 16 hr. 50 min. | +0.47° | +10.64° |
| 22 min. | +2.35° | +53.40° | 22 hr. 50 min. | +0.52° | +11.82° |
| 24 min. | +2.30° | +52.26° | 26 hr. 35 min. | +0.52° | +11.82° |
| 26 min. | +2.25° | +51.13° | 47 hr. 50 min. | +0.62° | +14.09° |
| 35 min. | +1.97° | +44.77° | 3 days 18 hr. | +0.76° | +17.27° |
| | | | 7 days 21 hr. | +0.90° | +20.45° |

From this table it is clear that *d*-gluconic β -lactone is converted in
two and one-half hours at 20° to the extent of nearly 80% into free *d*-glu-
conic acid ($[\alpha]_D^{20} = -1.7^\circ$). It should be especially noticed that tem-
porary equilibrium was maintained with $[\alpha]_D^{20} = +11^\circ$ for 24 hrs.²

¹ *Ann.*, 403, 325 (1914).

² According to Nef (*Ann.*, 403, 326 (1914)) aqueous solutions of β -lactone reach
 $[\alpha]_D^{20} = +9.94^\circ$ after 2½ hrs. standing at 20°; $[\alpha]_D^{20} = +7.71^\circ$ after 4½ hours; a
minimum at $[\alpha]_D^{20} = +6.24^\circ$ after 26 hrs.; $[\alpha]_D^{20} = +7.95^\circ$ after 46 hrs.; $[\alpha]_D^{20} =$
+6.69° after 70 hrs.; and $[\alpha]_D^{20} = +9.94^\circ$ after 114 hrs.

Dr. Nef suggests that the values for the specific rotation lower than +9.94° may
be inaccurate due to fatigue of his research assistant's eyes.

Final equilibrium at 20° in 4% aqueous solutions of *D*-gluconic acid, as well as of β - and γ -lactones, is, however, only reached, when the specific rotation has become about +18° (see below). Such solutions, heated for five hours on a boiling water bath and then quickly cooled, give at first a specific rotation of +32° to +34°, which changes on long standing to about +18°.

Thus, a solution of 0.5748 g. β -lactone in 14.8255 g. H₂O, heated for one hour on a boiling water bath and then cooled rapidly, gave $[\alpha]_D^{20} = +28.89^\circ$ ($\alpha = +1.09^\circ$ in a 1 dc. tube); $[\alpha]_D^{20}$ fell to +25.17° after 2³/₄ hrs., and to +23.05° after 24 hrs. standing at room temperatures. In a second experiment a solution of 0.5075 g. β -lactone in 13.0649 g. H₂O, heated for five hours on a boiling water bath and cooled rapidly, gave $[\alpha]_D^{20} = +32.51^\circ$ ($\alpha = +1.23^\circ$ in a 1 dc. tube); $[\alpha]_D^{20}$ fell to +26.91° after 16³/₄ hrs. and to +17.72° after 15¹/₂ days standing at room temperatures. This solution must have contained at first ($[\alpha]_D^{20} = +32.51^\circ$) about 50% of β - and γ -lactones of which 8 to 12% was β -lactone, for an aqueous solution, originally containing pure *D*-gluconic γ -lactone (cf. Table V), gave, after standing 4³/₄ days at room temperatures, $[\alpha]_D^{20} = +33.98^\circ$; this fell to +26.46° after 48 hrs. further standing at room temperatures.

It is consequently obvious from the data presented that the situation here is entirely analogous to that observed in the case of free *D*-mannonic acid and its β -lactone. An aqueous solution of free *D*-gluconic acid (see below) or of *D*-gluconic β -lactone rapidly reaches an equilibrium with the specific rotation +10° or +11°; since, however, abnormal γ -lactone formation also takes place, but extremely slowly at 20°, there is a gradual rise in the specific rotation of such solutions until a limit is reached with $[\alpha]_D^{20} = +18^\circ$. There is in the present case no irreversible and complete transformation into γ -lactone, because *D*-gluconic γ -lactone is, in contrast to *D*-mannonic γ -lactone, slowly acted upon by water at 20°.

Ethyl *D*-Gluconate.—This ester crystallizes from absolute alcohol, in which it is very soluble, in bulky, fibrous needles; these contain, air-dried, much alcohol of crystallization and melt from 40–50°; after standing over H₂SO₄ *in vacuo*, they lose the alcohol and melt between 62° and 63°. I observed no optical activity in a 4% aqueous solution of the ester, whereas Nef¹ obtained $[\alpha]_D^{20} = -0.997^\circ$.

The ester is formed by the addition of ethyl alcohol to the active molecules of *D*-gluconic β -lactone (cf. ethyl *D*-mannonate) in the presence of small quantities of the free *D*-gluconic acid or hydrogen chloride. In many experiments large amounts of ester were obtained by dissolving a residual gum, consisting of *D*-gluconic acid and of β - and γ -lactones, in boiling absolute alcohol, whereupon the alcohol was removed at reduced pressure, until a thin syrup remained; this would then, on standing, be spontaneously

¹ *Ann.*, 403, 327 (1914).

transformed into a mass of crystals of γ -lactone and of ethyl ester, which could easily be separated by fractionation from absolute alcohol.

The ethyl ester was also obtained in the following definite way: A solution of free *d*-gluconic acid, obtained from 9.53 g. anhydrous calcium *d*-gluconate and 2.73 g. crystallized oxalic acid, was digested a few moments on a boiling water bath, cooled, and filtered free from calcium oxalate. The water was removed from the filtrate by distillation at 20 mm. pressure, with the residue standing over CaCl_2 . The residual gum, 7.13 g., was heated for five hours at 150° (5.21 g.) dissolved, on shaking, in 100 cc. of cold absolute alcohol; after concentration to about 25 cc., one drop of 17.25 *N* alcoholic hydrogen chloride was added to this solution, which was then warmed to 50° for about 3 mins., whereupon it was cooled by running water. After standing 20 hrs., 1.25 g. ethyl ester, melting (after drying over H_2SO_4 *in vacuo*) between 62° and 63° , separated out.

Analysis and physical constants of ethyl *d*-gluconate:

0.1997 g. gave 0.3123 g. CO_2 and 0.1267 g. H_2O .

Calc. for $\text{C}_8\text{H}_{16}\text{O}_7$: C, 42.83; H, 7.20; found: C, 42.65; H, 7.12.

The molecular weight of β -lactone, determined by the boiling point method in McCoy's apparatus (see above) using 0.5811 g. substance dissolved in absolute alcohol, was found to be 252 instead of 224 calculated for $\text{C}_8\text{H}_{16}\text{O}_7$.

| | | | |
|-----------------------|---------------|---------------|---------------|
| Vol. of solution, cc. | 25.0 | 30.6 | 31.3 |
| Rise in B. P. | 0.141° | 0.120° | 0.115° |
| Mol. wt. found. | 257 | 247 | 252 |
| | | | Av. 252 |

No optical activity was observed at first on dissolving 0.57 g. ethyl ester in 12.48 g. H_2O ; the solution became optically active, however, on standing at room temperatures through hydrolysis of the ester and subsequent conversion of free *d*-gluconic acid into β - and γ -lactones.

| Time after solution. | Observed angle. | $[\alpha]_D$. |
|----------------------|-----------------|----------------|
| 6 days | $+0.35^\circ$ | $+7.60^\circ$ |
| 10 days | $+0.46^\circ$ | $+9.98^\circ$ |
| 17 days | $+0.50^\circ$ | $+10.85^\circ$ |

If the specific rotation at the end of 17 days be calculated on the basis of lactone produced by hydrolysis (0.57 g. ester gives 0.453 g. lactone), it becomes $+14.25^\circ$, which is in fairly close agreement with the region of equilibrium, $+18^\circ$, reached by aqueous solutions of free *d*-gluconic acid and of *d*-gluconic β - and γ -lactones on long standing at ordinary temperatures.

The following further experiments with ethyl *d*-gluconate are interesting since they show that the β -lactone can be obtained from the ester to the extent of about 30% by simply heating in a distilling flask under 20 mm. pressure in a bath kept between 70° and 80° for 10 hrs.; a small amount of polygluconic anhydrides is also formed, as well as some γ -lactone. The γ -lactone could probably be obtained to the extent of 70% or more

by raising the temperature of the surrounding bath to 130–140° during the experiment. Thus, after 3 g. of ethyl *D*-gluconate had been heated at 70–80° as described, with a loss in weight of 0.52 g., a partly crystalline mass remained in the distilling flask from which 1.03 g. crude β -lactone, melting from 140–152°, were obtained. In a second experiment 3.7 g. ester lost 0.55 g. in weight; the residual partly crystalline mass yielded 0.94 g. β -lactone melting from 152–153.5°.

***D*-Gluconic Acid.**—This acid, $C_6H_{12}O_7$, has been obtained only as a syrup ($[\alpha]_D^{20} = -1.7^\circ$), very soluble in absolute alcohol, and is transformed in aqueous solution at ordinary temperatures mainly into β -lactone, but at 100° largely into γ -lactone; at all temperatures, however, equilibrium is established in aqueous solution with a definite percentage of these three components present.

In order to determine when equilibrium is reached in aqueous solutions at 20°, *D*-gluconic acid was prepared from a warm (60°) aqueous solution of 10 g. anhydrous calcium *D*-gluconate (corresponding to 9.19 g. $C_6H_{12}O_7$) by treatment with 2.93 g. crystallized oxalic acid in water also at 60°. Immediately after mixing, the solution of *D*-gluconic acid was cooled within one minute to 20°, filtered from calcium oxalate, and made up to 250 cc.; it gave $[\alpha]_D^{20} = +2.19^\circ$ (calculated for $C_6H_{12}O_7$) forty-five minutes after cooling ($\alpha = +0.16^\circ$ in a 2 dc. tube; $c = 3.647$). The following subsequent observations were made with the same tube kept at room temperatures. The calculations for the specific rotation are here, however, based on the theoretical amount of lactone, 8.28 g., obtainable from 10 g. anhydrous calcium *D*-gluconate. Equilibrium was finally reached with the specific rotation about $+18^\circ$.

TABLE IV.

| Time after cooling the solution. | Observed angle. | $[\alpha]_D$. |
|----------------------------------|-----------------|----------------|
| 45 min. | $+0.16^\circ$ | $+2.42^\circ$ |
| 2 hrs. | $+0.45^\circ$ | $+6.80^\circ$ |
| 20 hrs. | $+0.65^\circ$ | $+9.82^\circ$ |
| 1 day 23 hrs. | $+0.65^\circ$ | $+9.82^\circ$ |
| 3 days | $+0.77^\circ$ | $+11.63^\circ$ |
| 4 days | $+0.81^\circ$ | $+12.24^\circ$ |
| 5 days | $+0.96^\circ$ | $+14.50^\circ$ |
| 7 days | $+1.05^\circ$ | $+15.85^\circ$ |
| 11 days | $+1.17^\circ$ | $+17.67^\circ$ |

From Table IV it is evident that a condition of temporary equilibrium was maintained with the specific rotation at about $+10^\circ$ for 27 hrs.; this is in fairly close agreement with the region of temporary equilibrium ($+11^\circ$), reached after an aqueous solution of *D*-gluconic β -lactone (see above) has stood for two and one-half hours at ordinary temperatures.

According to observations published by Schnelle and Tollens,¹ an

¹ *Ann.*, 271, 74 (1890); *Ber.*, 23, 2991 (1890).

aqueous solution of free *d*-gluconic acid reaches equilibrium with the specific rotation between $+10^\circ$ and $+12^\circ$ after standing two or three weeks at room temperatures.

Equilibrium at $96-98^\circ$ was found thus: a solution of *d*-gluconic acid, prepared from 10 g. anhydrous calcium *d*-gluconate (corresponding to 8.28 g. lactone), was heated for $13\frac{1}{2}$ hrs. on a boiling water bath; quickly cooled this gave $[\alpha]_D^{20} = +32.46^\circ$ calculated on the basis of $C_6H_{10}O_6$, ($\alpha = +2.14^\circ$ in a 2 dc. tube; $c = 3.312$); $[\alpha]_D^{20}$ fell to $+25.52^\circ$ after $15\frac{1}{2}$ hrs. and to $+17.96^\circ$ after 16 days' standing at room temperatures. *d*-Gluconic β -lactone as well as far more γ -lactone must have been present at the end of $13\frac{1}{2}$ hrs. heating.

***d*-Gluconic γ -Lactone.**—This abnormal lactone has been obtained by E. Fischer¹ in practically pure condition. He recrystallized the lactone twice from small amounts of water and found that it melted between 130° and 135° , and gave $[\alpha]_D^{20} = +68.2^\circ$ in 8% concentration, or after 24 hrs. standing $+64.13^\circ$. No β -lactone could therefore have been present. Schnelle and Tollens² describe a preparation, melting from 122° to 125° , which gave $[\alpha]_D^{20} = +61.59^\circ$ ten minutes after solution, and eight minutes later $+58.83^\circ$, in about 8% concentration; therefore a small amount of β -lactone was present. Nef³ found the melting point of a preparation of pure γ -lactone, twice crystallized from 14 parts of absolute alcohol, to be $133-135^\circ$ with $[\alpha]_D^{20} = +67.82^\circ$ (in 4% concentration). I obtained γ -lactone, recrystallized from eight parts of absolute alcohol, melting from 134° to 136° with $[\alpha]_D^{20} = +67.52^\circ$ (in 4% concentration).

Many experiments were carried out to determine the best conditions for obtaining the γ -lactone; the best of these with the results follow. When a solution of *d*-gluconic acid, of slightly less than 4% concentration, was heated for $13\frac{1}{2}$ hrs. on a boiling water bath (cf. *d*-gluconic acid), the specific rotation became $+32.46^\circ$, indicating the presence of a large amount, perhaps 45 to 50%, of γ -lactone, besides a much smaller amount of β -lactone.

In another experiment the aqueous filtrate, obtained from 26.33 g. anhydrous calcium *d*-gluconate (corresponding to 21.8 g. lactone) by treatment with the calculated amount of crystallized oxalic acid, 7.115 g., was heated for only one hour on a boiling water bath and then allowed to reach room temperature by standing one hour longer, with final cooling at 20° . This filtrate made up to 640 cc. with water gave $[\alpha]_D^{20} = +16.99^\circ$, calculated on the basis of $C_6H_{10}O_6$ ($\alpha = +1.21^\circ$ in a 2 dc. tube; $c = 3.406$). The water was now removed from the solution 20 hrs. later by distillation at 20 mm. pressure with the surrounding bath at 50° , until no more mois-

¹ *Ber.*, **23**, 2625 (1890).

² *Ann.*, **271**, 76 (1892).

³ *Ibid.*, **403**, 330 (1914).

ture condensed in the neck of the flask, whereupon the gum, 21.3 g., gave $[\alpha]_D^{20} = +22.94^\circ$, calculated on the basis of $C_6H_{10}O_6$ ($\alpha = +2.00^\circ$ in a 2 dc. tube; $c = 4.26$); $[\alpha]_D^{20}$ fell to $+17.77^\circ$ after 50 hrs. standing at room temperatures. The amount of lactone in the gum was therefore very little more than that in solution before the above distillation. After removing the water again by distillation at 20 mm. pressure with the surrounding bath at 70° , the residual gum, heated two hours longer at 90° , now weighed 19.5 g. and gave $[\alpha]_D^{20} = +52.82^\circ$, calculated on the basis of $C_6H_{10}O_6$, fifteen minutes after solution ($\alpha = +10.3^\circ$ in a 2 dc. tube; $c = 9.75$); this fell to $+28.72^\circ$, after standing 19 hrs. at room temperatures, showing that, besides a large amount of γ -lactone, much β -lactone was present.

These data make it perfectly clear that the most ideal way, in which to obtain a maximum yield of *D*-gluconic γ -lactone from anhydrous calcium *D*-gluconate, is to precipitate the calcium with the calculated amount of crystallized oxalic acid, and thereupon to heat the aqueous solution of free *D*-gluconic acid for 12 hrs. on a boiling water bath. At least 50% of the acid will be transformed into the β - and γ -lactones. The water must then be removed by distillation at 50 mm. pressure, while the temperature of the surrounding bath is kept between 90° and 100° . In this way at least 80% of γ -lactone should be obtained.

An attempt to prepare γ -lactone by heating a residual gum *in vacuo* to 130° proved successful. Under these conditions a larger amount than usual was produced. Thus, an aqueous solution of *D*-gluconic acid, prepared from 15 g. anhydrous calcium *D*-gluconate by treatment with 4.4 g. crystallized oxalic acid, was heated for one hour on a boiling water bath and filtered from calcium oxalate. The water was removed from the filtrate by distillation at 20 mm. pressure with the surrounding bath at 45° , whereupon the syrup was heated in an oil-bath at 130° for $4\frac{1}{2}$ hrs. The residual light brown gum, 11.58 g., was resolved by 200 cc. boiling absolute alcohol into two portions, A, 2.98 g. insoluble polygluconic anhydrides, and B, 8.6 g. soluble gum which dissolved in 50 cc. absolute alcohol yielded 1.98 g. crude γ -lactone, melting from 133° to 137° , with $[\alpha]_D^{20} = +67.05^\circ$ (seven minutes after solution); this fell to $+55.66^\circ$ after five hours' standing at room temperatures. There was, therefore, a small amount of β -lactone present (cf. rate of change of β - and γ -lactones).

E. Fischer and others have analyzed *D*-gluconic γ -lactone; therefore only the following additional data on this substance were ascertained:

0.4761 g., dissolved in excess of 0.1 *N* KOH heated 10 mins. on a boiling water bath and titrated back with 0.1 *N* H_2SO_4 , used 26.84 cc. 0.1 *N* KOH instead of 26.75 cc. calculated for $C_6H_{10}O_6$.

A molecular weight determination by the boiling point method with 0.5720 g. γ -lactone dissolved in absolute alcohol, using McCoy's apparatus (see above) gave 194 instead of 178 calculated for $C_6H_{10}O_6$.

| | | | | | |
|---------------------------|--------|--------|--------|--------|---------|
| Vol. of solution, cc..... | 27.3 | 28.4 | 29.5 | 30.8 | |
| Rise in B. P..... | 0.169° | 0.161° | 0.154° | 0.151° | |
| Mol. wt. found..... | 193 | 195 | 196 | 191 | Av. 194 |

The specific rotation of *d*-gluconic γ -lactone was found to be $+67.52^\circ$ at 20° nine minutes after solution (0.4190 g. in 9.8876 g. H_2O gave $\alpha = +2.78^\circ$ in a 1 dc. tube). The following subsequent observations were made with the same tube kept at room temperatures:

TABLE V.

| Time after solution. | Observed angle. | $[\alpha]_D$. |
|----------------------|-----------------|----------------|
| 50 min. | $+2.78^\circ$ | $+67.52^\circ$ |
| 18 hrs. | $+2.42^\circ$ | $+58.75^\circ$ |
| 21 hrs. | $+2.42^\circ$ | $+58.75^\circ$ |
| 2 days 18 hrs. | $+1.83^\circ$ | $+44.43^\circ$ |
| 3 days 18 hrs. | $+1.57^\circ$ | $+38.12^\circ$ |
| 4 days 18 hrs. | $+1.40^\circ$ | $+33.98^\circ$ |
| 6 days 18 hrs. | $+1.09^\circ$ | $+26.46^\circ$ |
| 7 days 18 hrs. | $+0.98^\circ$ | $+23.79^\circ$ |
| 9 days 18 hrs. | $+0.83^\circ$ | $+20.15^\circ$ |
| 10 days 22 hrs. | $+0.78^\circ$ | $+18.94^\circ$ |
| 13 days 22 hrs. | $+0.72^\circ$ | $+17.69^\circ$ |

Another experiment with 1.00015 g. γ -lactone dissolved in 24.0751 g. H_2O gave $[\alpha]_D^{20} = +66.91^\circ$ twenty-five minutes after solution ($\alpha = +5.398^\circ$ in a 2 dc. tube); this fell to $+66.40^\circ$ and to $+58.35^\circ$ after standing at room temperatures for $2\frac{1}{4}$ hrs. and 24 hrs. after solution, respectively.

d-Gluconic γ -lactone reacts rapidly with water at higher temperatures; such a solution, after heating 10 hrs. at 98° , reaches equilibrium at about $+34^\circ$, as is evident from the following data: these are, moreover, in perfect agreement with the results of heating *d*-gluconic β -lactone and *d*-gluconic acid in aqueous solutions.

A solution of 0.8706 g. γ -lactone in 20.1144 g. H_2O , heated for one hour on a boiling water bath, gave, on rapid cooling to 20° , $[\alpha]_D^{20} = +40.53^\circ$ ($\alpha = +1.7^\circ$ in a 1 dc. tube); this fell to $+37.92^\circ$, to $+33.86^\circ$ and to $+18.09^\circ$ after standing 1 hr., $14\frac{1}{2}$ hrs. and 19 days, respectively, at room temperatures. Another solution of 0.4441 g. γ -lactone in 10.1686 g. H_2O , heated for five hours on a boiling water bath and then cooled rapidly, gave $[\alpha]_D^{20} = +35.09^\circ$ ($\alpha = +1.48^\circ$ in a 1 dc. tube); this fell to $+28.36^\circ$ and to $+25.76^\circ$ after standing $1\frac{1}{8}$ hrs. and $20\frac{1}{2}$ hrs., respectively, at room temperatures. A third solution of 0.4239 g. γ -lactone in 9.7897 g. H_2O , heated for ten hours on a boiling water bath, gave, on rapid cooling to 20° , $[\alpha]_D^{20} = +34.84^\circ$ ten minutes after cooling ($\alpha = +1.48^\circ$ in a 1 dc. tube); this fell to $+27.07^\circ$ and to $+18.12^\circ$ after standing 18 hrs. and 17 days, respectively, at room temperatures.

The change in optical activity between $+34.84^\circ$ and $+27.07^\circ$ (during

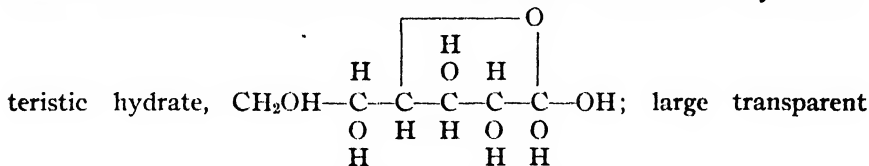
18 hrs.) is more rapid than the change, observed with an aqueous solution of pure *d*-gluconic γ -lactone (cf. Table V) at 20°, between +33.98° and +26.46° (during 48 hrs.); therefore considerable β -lactone must have been present.

Finally, Schnelle and Tollens¹ published long ago some observations on a crystalline lactone, obtained from free *d*-gluconic acid, to which they assign the composition $C_{12}H_{22}O_{11}$ or $C_{12}H_{20}O_{11}$. Their preparation melted between 110° and 115° and gave $[\alpha]_D^{20} = +39.07^\circ$, or +14.84° after standing at 19° for 52 days. 1.017 g. substance lost 0.078 g. in weight assumed without proof to be water. It is now very obvious that their product simply consisted of mixed crystals of ethyl *d*-gluconate (about 57%) and *d*-gluconic γ -lactone. Nef, as well as I, has repeatedly obtained such low melting mixed crystals which could always be resolved into the two components by further recrystallization from alcohol.

III. Ortho-bis-*d*-Galactonic Acid, *d*-Galactonic γ -Lactone and Its Monohydrate.

All attempts to prepare an ester and a monomolecular β -lactone of *d*-galactonic acid, analogous to those in the *d*-mannonic acid and *d*-gluconic acid series, have failed, although some slight evidence of the existence of a β -lactone, rapidly decomposed by water has been obtained (see below). Kohn² has prepared ethyl *d*-galactonate in combination with calcium chloride.

Pure *d*-galactonic γ -lactone, opaque prismatic needles, melting between 108° and 111° with $[\alpha]_D^{20} = -76.97^\circ$, has been prepared. This lactone is remarkable for the ease with which it adds water to form the very charac-



prisms, melting at 66° with $[\alpha]_D^{20} = -70.1^\circ$, analogous to chloral hydrate and bis-ortho oxalic acid. Both of these compounds are very soluble in water and in alcohol, but with some difficulty in ethyl acetate.

Free *d*-galactonic acid, on the other hand, is, in very marked contrast to *d*-mannonic and *d*-gluconic acids, a solid [melting between 140° and 141°, with $[\alpha]_D^{20}$ (calculated as $C_6H_{12}O_6$, see below) = -12.23°] practically insoluble in boiling absolute alcohol. It contains one-half a molecule of water of crystallization which can not be removed by prolonged drying over H_2SO_4 *in vacuo*. I therefore name it ortho-bis-*d*-galactonic acid and assign to it the bimolecular formula, $C_6H_{12}O_7 \cdot CH_2OH(CHOH)_4C(OH)_3$,

¹ *Ann.*, 271, 79 (1892).

² *Monats.*, 16, 334 (1895).

analogous to bis-ortho oxalic acid, or the more stable milk sugar hydrates, $\text{CH}_2(\text{OH})\text{CHOHCH}(\text{CHOH})_2\text{—C—O—CH}_2(\text{CH}_2\text{CH}(\text{OH})_2)_2$

etc. It is monomolecular in cold aqueous solutions, and titrates with alkali hydroxides, therefore, at once in the cold for free *d*-galactonic acid.

Ortho-bis-*d*-Galactonic Acid.—This acid has already been isolated in an impure condition (melting between 122° and 125°) over 30 years ago by Kiliani,¹ and his observations have been confirmed by Schnelle and Tollu.² The latter authors have also succeeded in raising the melting point of the acid by crystallization from water with the addition of alcohol.

I prepared the pure acid in the following way: An aqueous solution of 97.2 g. calcium *d*-galactonate (containing 4 H₂O by analysis) was treated on a boiling water bath with the calculated amount of crystallized oxalic acid, 24.4 g., in water and, after five minutes' digestion, the mixture, cooled quickly with running water, was filtered free from calcium oxalate. When the filtrate had become concentrated by distillation at 20 mm. pressure with the surrounding bath never over 50°, crystals of ortho-bis-*d*-galactonic acid separated out in large amounts; 26.79 g. of crude acid, melting between 122° and 125°, were thus obtained in two crops. These were dissolved in 77 cc. water at 60° and the filtrate was then poured into 500 cc. absolute alcohol with subsequent addition of 200 cc. absolute alcohol; 17.48 g. crystal needles (melting at 140–141°, with $[\alpha]_D^{20}$ (calculated on the basis of C₆H₁₂O₇) = –12.23°) separated out on standing. The water-alcohol filtrate, concentrated to 50 cc. at reduced pressure, yielded, on addition of 100 cc. absolute alcohol, 4.17 g. of equally pure acid.³

The acid loses water with great difficulty for 0.9818 g., air-dry crystals, melting at 140–141°, kept over H₂SO₄ *in vacuo*, lost only 0.0041 g. H₂O after 20 days.

Six analyses of five preparations of the substance were made; one preparation was crystallized from water alone, and the others from water and varying amounts of alcohol; the melting points of the acid obtained ranged, after drying over H₂SO₄ *in vacuo*, from 134–147°.

¹ *Ber.*, 14, 651 (1881); *Ibid.*, 18, 1551 (1885).

² *Ann.*, 271, 82 (1892).

³ *Ber.*, 33, 2146 (1900).

⁴ *Ann.*, 403, 273–275 (1914).

⁵ The mother liquor, still containing 5.1 g. substance, was united with the original aqueous filtrate from which 26.79 g. crude acid had been removed, and the combined solutions were worked up for *d*-galactonic γ -lactone and γ -lactone hydrate (see below).

| | Gram. | M. p. | CO ₂ . | H ₂ O. | % C. | % H. |
|-----|---------|--------|-------------------|-------------------|-------|------|
| I | 0.3168 | 140-1° | 0.4051 g. | 0.1837 g. | 34.88 | 6.39 |
| II | 0.36375 | 140-1° | 0.4680 g. | 0.2143 g. | 35.09 | 6.54 |
| III | 0.3199 | 147° | 0.4105 g. | 0.1837 g. | 35.00 | 6.38 |
| IV | 0.3571 | 143-4° | 0.4591 g. | 0.2066 g. | 35.06 | 6.43 |
| V | 0.3443 | 136-8° | 0.4416 g. | 0.1947 g. | 34.98 | 6.35 |
| VI | 0.3235 | 134-6° | 0.4125 g. | 0.1850 g. | 34.77 | 6.35 |

Calc. for C₁₂H₂₀O₁₃ 35.11 6.49

On titration with 0.1 *N* sodium hydroxide in the cold the substance behaved like a free acid; 0.4247 g. used 20.20 cc. 0.1 *N* NaOH (phenolphthalein) instead of 20.69 cc. calculated for C₁₂H₂₀O₁₃.

A molecular weight determination by the freezing point method proved that the acid, in cold aqueous solutions, is monomolecular, *i. e.*, such solutions contain either free meta *D*-galactonic acid or free ortho *D*-galactonic acid (molecular weights 196 and 214, respectively), or perhaps both. 1.1506 g. substance were used. The phenomenon of supercooling was considered in the usual way and the amount of liquid solvent, *W'*, was found by the formula

$$W' = W(1 - \frac{S.D}{L}),$$

in which *W* is the total solvent (24.879 g. H₂O), *S* is the specific heat of the solvent, *L* is the latent heat of fusion, and *D* is the supercooling.

| D'. | W'. | Δ. | Mol. wt. found. ¹ |
|-------|---------------------------|--------|------------------------------|
| 0.184 | 24.84 g. H ₂ O | 0.442° | 194.9 |
| 1.674 | 24.12 g. H ₂ O | 0.447° | 198.4 |
| 1.663 | 24.38 g. H ₂ O | 0.448° | 195.9 |

Average, 196.4

The molecular weight determination was not corrected for ionization of the acid; this would be too small to make much increase in the observed molecular weight.

There was for a long time doubt on the question as to whether the formula of the crystalline acid was C₆H₁₂O₇·H₂O or 2C₆H₁₂O₇·H₂O, *i. e.*, whether the substance was ortho-*D*-galactonic acid or ortho-bis-*D*-galactonic acid. This was finally settled in favor of the latter formula by the following experiment: 5.06 g. ortho-bis-*D*-galactonic acid, melting at 140-141°, were heated for two hours in a small distilling flask under 20 mm. pressure with the surrounding bath at 145°; the flask was connected with a small condenser, which was joined to a receiver cooled to -16°. A slow, continuous stream of dry air was passed through the molten mass by means of a capillary tube. The amount of ice, which accumulated in the receiver, was 0.62 g. or 12.35%, whereas 0.665 g., or 13.17%, is the

¹ For preliminary practice the molecular weight of pure crystallized glucose by the freezing point method was found to be 176.7 instead of 180 for C₆H₁₂O₆.

theoretical amount of water, for $C_{12}H_{26}O_{15} = 3H_2O$. The molten distillate also gave no iodoform test, establishing the absence of alcohol. Finally the residue in the distillate, 4.29 g., yielded by crystallization from absolute alcohol 1.0383 g. of γ -lactone, melting from 105° to 109° .

Since ortho-bis-*d*-galactonic acid exists only in the monomolecular form in aqueous solution, it should show exactly the same specific rotation as an acid just liberated from a salt. This is a fact. I found $[\alpha]_D^{20} = -12.23^\circ$ (calculated on the basis of $C_6H_{12}O_7$) for the pure crystalline acid, melting at 140 – 141° , in a 4% aqueous solution. Schnelle and Tollens¹ found that the specific rotation of free *d*-galactonic acid, on liberation from its calcium salt by hydrochloric or oxalic acids, was -10.56° (calculated on the basis of $C_6H_{12}O_7$). Nef observed that the specific rotation of a 4% aqueous solution of a similarly liberated acid was -12.64° , six minutes after its preparation; this fell to -11.35° and rose again to -12.40° after standing for 10 and 22 1/2 hrs. respectively, at ordinary temperatures.

The specific rotation of aqueous solutions of ortho-bis-*d*-galactonic acid increase and reach a limit at about -50° , after standing about three weeks at ordinary temperatures, or in one hour at 100° (see below); this is due to a transformation of the acid mainly into the isomeric *d*-galactonic γ -lactone hydrate, melting at 66° , with $[\alpha]_D^{20} = -70.1^\circ$ (see below). Since, however, this lactone hydrate is also slightly acted upon by water, even at 20° , aqueous solutions of γ -lactone hydrate, or of ortho-bis acid, finally always contain a mixture of three substances in equilibrium, namely, 70 to 80% of γ -lactone hydrate, 30 to 20% of free acid, besides traces of the γ -lactone (see below).

1.0383 g. of ortho-bis-*d*-galactonic acid (corresponding to 0.9927 g. $C_6H_{12}O_7$) dissolved in 25.0781 g. H_2O , gave $[\alpha]_D^{20} = -12.23^\circ$, six minutes after solution ($\alpha = -0.94^\circ$ in a 2 dc. tube). The changes observed in the specific rotation of this solution on standing at ordinary temperatures follow:

TABLE VI.

| Time after solution. | Observed angle. | $[\alpha]_D$ calculated on basis of $C_6H_{12}O_7$. |
|----------------------|-----------------|--|
| 2 days 16 hrs. | -2.51° | -32.66° |
| 3 days 19 hrs. | -2.85° | -37.08° |
| 4 days 23 hrs. | -2.97° | -38.64° |
| 5 days 22 hrs. | -3.16° | -41.12° |
| 9 days 17 hrs. | -3.36° | -43.71° |
| 10 days 17 hrs. | -3.46° | -45.02° |
| 17 days 17 hrs. | -3.90° | -50.75° |

Another observation on the specific rotation of a preparation of ortho-bis-*d*-galactonic acid, which had been kept one year, gave $[\alpha]_D^{20} = -13.32^\circ$

¹ *Ann.*, 271, 85 (1892).

(calculated on the basis of $C_6H_{12}O_7$) i. e., 1.6143 g. *ortho*-bis-*D*-galactonic acid (corresponding to 1.544 g. $C_6H_{12}O_7$) dissolved in 36.1823 g. H_2O gave $\alpha = -1.10^\circ$ in a 2 dc. tube fourteen minutes after solution. Subsequent changes in the optical activity of this solution are recorded in this table:

TABLE VII.

| Time after solution. | Observed angle. | $[\alpha]_D$ calculated on the basis of $C_6H_{12}O_7$. |
|----------------------|-----------------|--|
| 2 hrs. 25 min. | -0.95° | -11.50° |
| 3 hrs. 25 min. | -0.89° | -10.78° |
| 5 hrs. 40 min. | -0.89° | -10.78° |
| 7 hrs. 25 min. | -0.89° | -10.78° |
| 11 hrs. 20 min. | -0.97° | -11.75° |
| 1 day | -1.22° | -14.78° |
| 2 days | -1.53° | -18.53° |
| 3 days 8 hrs. | -1.85° | -22.41° |
| 18 days | -3.76° | -45.54° |

The slight drop at first observed in the specific rotation of an aqueous solution of *ortho*-bis-*D*-galactonic acid (from -11.50° to -10.78°) possibly indicates the presence of a plus-rotating β -lactone, which is very unstable in aqueous solution (see below). Similar changes were invariably noticed in the case of freshly prepared aqueous solutions of *D*-galactonic acid, when set free from its salts by acids. Ten grams of calcium *D*-galactonate ($Ca(C_6H_{11}O_7)_2 \cdot 4H_2O$ by analysis) for example were dissolved in 150 cc. H_2O and treated with 2.51 g. oxalic acid in water at 60° . After shaking a few seconds, the solution was cooled in one-half minute to 20° and filtered from calcium oxalate. The filtrate (containing by calculation 7.81 g. free *D*-galactonic acid, $C_6H_{12}O_7$) was made up to 250 cc. with water and gave $[\alpha]_D^{20} = -7.68^\circ$ one hour after precipitation of the calcium oxalate ($\alpha = -0.48^\circ$ in a 2 dc. tube). The following table gives the subsequent changes in the optical activity of this solution, kept at ordinary temperatures:

TABLE VIII.

| Time after precipitation. | Observed angle. | $[\alpha]_D$ calculated on the basis of $C_6H_{12}O_7$. |
|---------------------------|-----------------|--|
| 3 hrs. 40 min. | -0.61° | -9.76° |
| 22 hrs. 15 min. | -1.33° | -21.29° |
| 1 day 22 hrs. 40 min. | -1.90° | -30.40° |
| 4 days 7 hrs. | -2.72° | -43.52° |
| 19 days 6 hrs. | -3.20° | -51.20° |
| 23 days 2 hrs. | -3.22° | -51.52° |

An aqueous solution of 1.0803 g. *ortho*-bis-*D*-galactonic acid (corresponding to 1.033 g. $C_6H_{12}O_7$), dissolved in 26.2848 g. H_2O , heated for one hour on a boiling water bath and cooled quickly to 20° , gave $\alpha = -1.85^\circ$ in a 1 dc. tube fifteen minutes after cooling; whence $[\alpha]_D^{20} = -48.51$ when calculated on the basis of lactone hydrate, $C_6H_{10}O_6 \cdot H_2O$. The

following, first a rise in specific rotation of the solution on standing at room temperature, and then a notable rise in specific rotation and a subsequent fall back to -49.0° .

| Time after cooling. | Observed angle. | $[\alpha]_D$ calculated on the basis of $C_6H_{10}O_6 \cdot H_2O$. |
|---------------------|-----------------|---|
| 2 hrs. 45 min. | -2.05° | -53.74° |
| 20 hrs. | -2.10° | -55.05° |
| 4 days | -2.05° | -53.74° |
| 14 days | -1.90° | -49.82° |

***d*-Galactonic γ -Lactone and Its Monohydrate.**—Schnelle and Tollens¹ were the first to obtain crystallized *d*-galactonic γ -lactone hydrate, $C_6H_{10}O_6 \cdot H_2O$, but they did not assign to it a structural formula. They gave the melting point, 66° , and found $[\alpha]_D^{20} = -65.6^\circ$ five minutes after solution. According to later observations by Clowes and Tollens,² a preparation, crystallized from acetone, with the same melting point, 66° , gave $[\alpha]_D^{20} = -67.9^\circ$. After driving off water from the hydrate by a stream of warm air, a preparation of γ -lactone, still contaminated with hydrate, was obtained by them in the form of needles melting at 90° with $[\alpha]_D^{20} = -72.1^\circ$. A preparation, melting at 100° , obtained by Hlasiwetz and Barth³ as early as 1862, also contained some unchanged hydrate, since *d*-galactonic γ -lactone is a very hygroscopic substance. Furthermore, it is obvious that the low specific rotations, obtained by Tollens and his co-laborers for the γ -lactone and its hydrate, were due to the presence of a small amount of ortho-bis-*d*-galactonic acid, since it is difficult to convert this substance completely into the γ -lactone. This can only be done, as Nef has repeatedly observed, by prolonged heating of residues at 20 mm. pressure in a distilling flask in a bath at 100° . By operating in this way he has, for example, repeatedly converted calcium *d*-galactonate, by treatment with oxalic acid, etc., to the extent of over 90% of the theory into pure *d*-galactonic γ -lactone, *i. e.*, by subsequently crystallizing the residual gums from absolute alcohol. It was, however, always necessary to re-heat the gums left in the alcoholic filtrates at 100° and under 20 mm. pressure; and in fact at least three or four such operations were necessary in order to obtain a ninety per cent. yield of γ -lactone. Prepared⁴ in this way, the γ -lactone crystallizes in needles, which melt between 108° and 111° and always give a specific rotation in the neighborhood of -77° , or of -70° , if calculated on the basis of γ -lactone hydrate, which is ob-

¹ *Ann.*, 271, 81 (1892).

² *Ibid.*, 310, 166 (1900).

³ *Ibid.*, 122, 96 (1862).

⁴ It is clear that the preparation of *d*-galactonic γ -lactone recently described by Ruff and Franz, *Ber.*, 35, 948 (1902), possessing $[\alpha]_D^{20} = -77.61^\circ$, must be identical with my product; the high melting point given, 135° , is probably due to a typographical error.

viously the only natural basis (see below), since the latter substance is practically the only one present in aqueous solutions at 20°.

The best way of obtaining a pure preparation of *D*-galactonic γ -lactone hydrate is to place the powdered γ -lactone and the calculated amount of water side by side in dishes in a closed vessel; the water is completely absorbed after two days' standing, and the resulting addition product is thereupon crystallized from ethyl acetate (see below).

The following further experiments with *D*-galactonic γ -lactone, as well as with γ -lactone hydrate, are of especial interest since they confirm in a very decisive way many of the preceding statements.

The above mentioned aqueous, and aqueous-alcoholic, mother liquors, from which 17.48 g. and 4.17 g. pure ortho-bis-*D*-galactonic acid had separated out by crystallization (see footnote, p. 364), were now freed from alcohol and water by distillation at reduced pressure and the residue, about 50 g. in 500 cc. H₂O, was now heated at 40° for 25 hrs. The water was again removed by distillation at 20 mm. pressure with the surrounding bath at 40°, until no more moisture condensed in the neck of the flask. The residual gum, 49.2 g., dissolved in cold water and made up to 500 cc., gave $[\alpha]_D^{20} = -47.49^\circ$ ($\alpha = -9.34^\circ$ in a 2 dc. tube; $c = 9.84$). The water was now again removed by distillation at 20 mm. pressure with the bath at 40°. The residual gum, on digestion at 40° with 200 cc. absolute alcohol, left 5.15 g. crystalline material undissolved, which melted from 113° to 119°, and was insoluble in warm absolute alcohol. The filtrate, freed from alcohol by distillation at reduced pressure, gave a residue which was heated at 60° until bubbles ceased to appear in the melt. This gum was soon transformed on standing into a crystalline mass which, when carefully broken loose by a rod and removed from the flask with 25 cc. absolute alcohol, yielded 29.6 g. air-dry crude γ -lactone hydrate melting from 65° to 70° with $[\alpha]_D^{20} = -55.83^\circ$ (calculated on the basis of C₆H₁₂O₇). A considerable portion of this, 19.8 g., when dissolved in 50 cc. of warm absolute alcohol, gave 8.07 g. mixed crystals melting from 66° to 85°; these, after drying three days over H₂SO₄ *in vacuo*, weighed 7.77 g., melted from 108° to 111°, and consisted therefore of practically pure γ -lactone.

Four grams of the finely powdered *D*-galactonic γ -lactone (melting from 108° to 111°) and the theoretical amount of water, 0.405 g., were placed side by side in dishes in an air-tight vessel. The water disappeared within two days; and the solid now weighed 4.44 g. and melted between 65° and 70°, but, after standing for two days over H₂SO₄ *in vacuo*, again lost the combined water with a simultaneous rise in melting point up to 105° to 110°. The γ -lactone had, therefore, been transformed into the hydrate and again recovered unchanged. It is obvious from these data that the *D*-galactonic γ -lactone is a very hygroscopic substance, which

can, therefore, be obtained from solvents containing no water; this explains why the melting point found usually to range from 108° to 111° .

d-Galactonic γ -lactone is soluble in about 200 parts of boiling ethyl acetate and separates therefrom on standing in opaque needles. The γ -lactone hydrate crystallizes from this solvent in large transparent prisms.

1.48 g. mixed crystals of *d*-galactonic γ -lactone and hydrate were dissolved in 400 cc. boiling ethyl acetate; this, concentrated to 200 cc., yielded on standing 0.65 g. needles, melting from 90° to 105° ; these, dried over H_2SO_4 in *vacuo* for three days, melted at 109 – 111° with $[\alpha]_D^{20} = -76.97^{\circ}$ (calculated on the basis of $\text{C}_6\text{H}_{10}\text{O}_6$) consisting therefore of pure γ -lactone.

2.58 g. mixed crystals of γ -lactone and hydrate were dissolved in 350 cc. boiling ethyl acetate; this solution on standing yielded 1.5 g. large transparent prisms, melting at 65 – 67.5° (air-dried) with $[\alpha]_D^{20} = -70.1^{\circ}$ (calculated on the basis of $\text{C}_6\text{H}_{10}\text{O}_6 \cdot \text{H}_2\text{O}$). This was pure *d*-galactonic γ -lactone hydrate. There must, therefore, be enough water in ordinary ethyl acetate to transform the γ -lactone into the hydrate. In a special experiment 0.5 g. *d*-galactonic γ -lactone, melting from 100° to 110° ; dissolved in 75 cc. boiling ethyl acetate, gave, on concentration to two-thirds the original volume, a considerable amount of gum on standing; this slowly and completely became transformed into large transparent prisms of γ -lactone hydrate melting from 64° – 67° .

Finally there are appended here data (physical, analytical, etc.) which were obtained with *d*-galactonic γ -lactone and its hydrate.

***d*-Galactonic γ -lactone.**—0.5721 g. substance, heated 10 min. on a boiling water bath with an excess of 0.1 *N* KOH, cooled and titrated back with 0.1 *N* H_2SO_4 , etc., used 32.01 cc. 0.1 *N* KOH (phenolphthalein) for neutralization instead of 32.12 cc. calculated for $\text{C}_6\text{H}_{10}\text{O}_6$.

A molecular weight determination with 0.5602 g. substance in boiling absolute alcohol using McCoy's apparatus (*Loc. cit.*) gave as the average molecular weight 192.3 instead of 178 calculated for $\text{C}_6\text{H}_{10}\text{O}_6$.

| | | | | | |
|----------------------------|-----------------|-----------------|-----------------|-----------------|-----------|
| Vol. of solution, cc. | 24.3 | 29.0 | 31.3 | 33.0 | |
| Rise in B. P. | 0.184° | 0.156° | 0.148° | 0.137° | |
| Mol. wt. found. | 195 | 193 | 188 | 193 | Av. 192.3 |

The specific rotation of pure γ -lactone was found to be -76.97° , or better -69.88° , when calculated on the basis of γ -lactone hydrate, since obviously this is practically the only substance present at first in a fresh aqueous solution, *i. e.*, 0.3464 g. substance and 9.0443 g. H_2O gave $\alpha = -2.87^{\circ}$ in a 1 dc. tube eight minutes after solution. The solution then underwent the following changes on standing at ordinary temperatures:

TABLE IX.

| Time after solution. | Observed angle. | $[\alpha]_D$ specific rotation for lactone hydrate. |
|----------------------------|-----------------|---|
| 20 hrs. | -2.79° | -67.92° |
| 4 days $4\frac{1}{2}$ hrs. | -2.73° | -66.45° |
| 9 days 1 hr. | -2.52° | -61.33° |
| 13 days 19 hrs. | -2.41° | -58.65° |
| 14 days 19 hrs. | -2.37° | -57.67° |
| 21 days 19 hrs. | -2.25° | -54.77° |
| 23 days 18 hrs. | -2.19° | -53.30° |
| 28 days 18 hrs. | -2.18° | -53.07° |
| 35 days 1 hr. | -2.03° | -49.41° |
| 44 days 19 hrs. | -1.98° | -48.20° |

d-Galactonic γ -Lactone Hydrate.—0.6450 g. required 32.72 cc. 0.1 *N* KOH for neutralization by the usual method (see above) instead of 32.91 cc. calculated from $C_6H_{10}O_6 \cdot H_2O$.

The specific solution of the γ -lactone hydrate was found to be -70.1° , *i. e.*, 0.3906 g. substance and 9.7905 g. H_2O gave $\alpha = -2.72^\circ$ in a 1 dc. tube ten minutes after solution. The solution then underwent the following changes at ordinary temperatures:

TABLE X.

| Time after solution. | Observed angle. | $[\alpha]_D$. |
|------------------------------|-----------------|----------------|
| $17\frac{3}{4}$ hrs. | -2.64° | -68.07° |
| 2 days $17\frac{1}{2}$ hrs. | -2.63° | -67.77° |
| 4 days 20 hrs. | -2.60° | -67.02° |
| 7 days $1\frac{1}{2}$ hrs. | -2.47° | -63.67° |
| 12 days 1 hr. | -2.32° | -59.80° |
| 16 days 20 hrs. | -2.25° | -58.00° |
| 24 days $20\frac{1}{2}$ hrs. | -2.20° | -56.70° |
| 26 days 18 hrs. | -2.14° | -55.15° |
| 31 days 18 hrs. | -2.08° | -53.68° |
| 38 days 1 hr. | -1.98° | -51.10° |
| 47 days 19 hrs. | -1.89° | -48.77° |

When *d*-galactonic γ -lactone is heated in a boiling water bath in 4% aqueous solution, equilibrium is quickly reached with the specific rotation between -58° and -61° , if the calculation is made on the only natural basis of $C_6H_{12}O_7$, which is the empirical formula of *d*-galactonic γ -lactone hydrate, as well as of free *d*-galactonic acid. This is decidedly higher than the specific rotations, about -48.5° (see above), finally reached by aqueous solutions of ortho-bis-*d*-galactonic acid, as well as of *d*-galactonic γ -lactone and its hydrate, and proves, as in all other instances (*cf.* *d*-mannonic and *d*-gluconic series), that more lactone (or lactone hydrate) is present in aqueous solution at higher temperatures. Thus, (A) a solution of 0.5363 g. *d*-galactonic γ -lactone in 11.7732 g. H_2O , heated for one hour on a boiling water bath and cooled quickly, gave $[\alpha]_D^{20} = -60.42^\circ$ *i. e.*, $\alpha = -2.93^\circ$ in a 1 dc. tube. (B) A second experiment with 0.5769

g. γ -lactone in 13.4041 g. H_2O , heated for five hours on a boiling water bath and cooled quickly gave $[\alpha]_D^{20} = -58.79^\circ$, *i. e.*, $\alpha = -2.75^\circ$ in a 1 dc. tube; curiously enough the specific rotation rose after 16 hours' standing at room temperatures to -59.87° . (C) A third experiment with 0.5035 g. γ -lactone in 11.9932 g. H_2O , heated on a boiling water bath for seven hours and cooled quickly, gave $[\alpha]_D^{20} = -59.54^\circ$, *i. e.*, $\alpha = -2.67^\circ$ in a 1 dc. tube. Here again a curious rise and subsequent fall in specific rotation were observed on standing at ordinary temperatures.

| Time after first reading. | Observed angle. | $[\alpha]_D$. |
|---------------------------|-----------------|----------------|
| 19 hrs. | -2.77° | -61.77° |
| 6 days | -2.54° | -56.63° |

It is clear from the data presented that aqueous solutions of ortho-bis-*d*-galactonic acid, or of *d*-galactonic γ -lactone or its hydrate, finally come to an equilibrium at 20° with $[\alpha]_D^{20} = -48.5^\circ$; at 100° , on the other hand, equilibrium is quickly reached with $[\alpha]_D^{20} = -60^\circ$. Such solutions contain 17 to 37% of free *d*-galactonic acid and 83 to 63% of *d*-galactonic γ -lactone hydrate (besides traces of γ -lactone) according to the temperature (between 20° and 100°) at which equilibrium occurs.

One might also draw the conclusion from the slight fluctuations at first noticed in the specific rotation of ortho-bis-*d*-galactonic acid, or of free *d*-galactonic acid when set free from its salts, as well as the curious fluctuations in specific rotation noticed after aqueous solutions of ortho-bis-*d*-galactonic acid and of *d*-galactonic γ -lactone have been heated at 100° and quickly cooled, that a faintly dextrorotatory *d*-galactonic β -lactone also exists in these solutions. All attempts, however, to isolate such a β -lactone, or even an ester of *d*-galactonic acid, were entirely fruitless.

I desire to express my gratitude to Dr. Nef for his painstaking instruction and constant aid in this work.

CHICAGO, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

SYNTHESES IN THE DIPHENYLMETHANE SERIES.

BY LAMBERT THORP AND E. A. WILDMAN.¹

Received December 11, 1914.

The work presented in this paper was undertaken with the idea of attempting to effect a synthesis of the hydrocarbon, fluorene, through the action of metals upon 2,2'-dibromodiphenylmethane. This latter substance was prepared by the elimination of the amino groups from 3,3'-diamino-6,6'-dibromodiphenylmethane, a compound which, in turn, had

¹ The work described in this article formed part of a thesis submitted for the degree of Master of Science to the graduate school of the University of Illinois by E. A. Wildman.

been obtained by acetylation and subsequent bromination of 3,3'-diaminodiphenylmethane.

In marked contrast to the usual ease with which, under the influence of sodium or other metals, ring formation occurs in the case of organic compounds halogenated in the 1,5-position, is the behavior of 2,2'-dibromodiphenylmethane under similar circumstances. Although sodium was allowed to act upon the dibromodiphenylmethane, both in anhydrous ether solution and in boiling xylene, and although the substance was subjected to the action of other metals, such as copper in the form of "Naturkupfer," and magnesium at temperatures up to 260°, the bromo-compound was in all cases recovered almost entirely unchanged, the only observed effect of the treatment being a slight reduction to diphenylmethane.

An interesting case of steric hindrance is observable in the behavior of hydroxylamine or of semicarbazine towards 2,2'-dibromobenzophenone, obtained by the oxidation of 2,2'-dibromodiphenylmethane. In the case of the former of these reagents several hours' boiling of the solution was insufficient to involve the ketone in reaction; and after being exposed to the action of semicarbazine for a month the ketone was recovered unchanged from the solution.

Experimental.

***m*-Nitrobenzyl Alcohol.**—In general the method of Becker¹ was followed, wherein *m*-nitrobenzaldehyde was subjected to the action of potassium hydroxide, in accordance with the well-known reaction of Cannizzaro. It was found advantageous, however, to saturate the alkaline solution with carbon dioxide before extracting the alcohol with ether. Under these circumstances the yield amounts to 92% of the theoretical.

3,3'-Dinitrodiphenylmethane.—This substance was first described by Gattermann and Rüdt² who prepared it by the condensation of *m*-nitrobenzylalcohol with nitrobenzene in the presence of sulfuric acid. In the same year, M. Schöpf³ obtained the compound through the action of formaldehyde upon nitrobenzene in sulfuric acid solution. Baeyer,⁴ employing, with slight modifications, the method of Gattermann and Rüdt, prepared the substance in 25% yield, the amount of tarry material formed at the same time being considerable.

At first, in our attempts to improve the yield by changing the conditions of condensation, 10 g. of *m*-nitrobenzylalcohol and 30 g. of nitrobenzene were dissolved in 200 cc. of concentrated sulfuric acid, and the solution allowed to remain at room temperature for 72 hrs. After the reaction mixture had been poured upon cracked ice it was observed that the amount

¹ *Ber.*, 15, 2090 (1882).

² *Ibid.*, 27, 2295 (1894).

³ *Ibid.*, 27, 2321 (1894).

⁴ *Ann.*, 354, 192 (1907).

of tarry material formed was negligible; hence it was unnecessary to purify the product by means of acetone, as recommended by Baeyer. The yield amounted to 20% of the theoretical.

Again, upon allowing the mixture to stand at room temperature for eleven days, the quantity of tar formed was very small, while the yield was increased to 25%.

After the solution of nitrobenzyl alcohol and nitrobenzene had remained on the water bath at a temperature of 95–97° for six hrs., the yield amounted to only 14%, while a similar treatment for 18 hrs. gave a 20% yield. Finally, after 48 hrs. at a temperature of 95–97°, the yield increased to 30%, the amount of tarry material being very slight. Accordingly, these conditions were adopted for the preparation of 3,3'-dinitrodiphenylmethane.

3,3'-Diaminodiphenylmethane.—This base was first prepared by M. Schöpf¹ from the corresponding dinitro-compound by reduction with stannous chloride. The yield, however, was poor. Better results were obtained with metallic iron and acetic acid.

Fourteen grams of 3,3'-dinitrodiphenylmethane were mixed in a porcelain dish with 30 g. of iron, in the form of powder, and 50 cc. of water. Two cubic centimeters of glacial acetic acid were added, and the mixture was then heated on the water bath, with constant stirring, until the reaction was apparently at an end. After about 2 hrs. further heating the greater part of the water had evaporated. The base was extracted with ether, the ethereal solution dried over potassium hydroxide, and the ether distilled. The product, which was obtained as a viscous oil, was immediately converted into its acetyl derivative.

3,3'-Diacetylaminodiphenylmethane.—The diamine, obtained as described above, was dissolved in 20 cc. of glacial acetic acid, and 15 cc. of acetic anhydride were added to the solution. Heat was evolved, and the reaction was brought to completion by warming the solution to its boiling point. The acetyl derivative, which separated in crystalline condition upon pouring the reaction mixture into cold water, was filtered with the aid of suction, and recrystallized from dilute alcohol. The yield was 13 g. or 83% of the theoretical, based upon the nitro compound.

3,3'-Diacetylaminodiphenylmethane crystallizes in the form of colorless leaflets, and has a melting point of 193°. It is readily soluble in alcohol or glacial acetic acid; slightly soluble in ether, benzene or ligroin; very slightly soluble in water.

0.2897 g. substance: 25.9 cc. N₂ (26°, 745 mm., over KOH).

Calc. for C₁₇H₁₈O₂N₂: N, 9.82; found: 9.90%.

3,3'-Diacetylamino-6,6'-dibromodiphenylmethane.—Twenty grams of 3,3'-diacetylaminodiphenylmethane were dissolved in 500 cc. of glacial

¹ Ber., 27, 2322 (1894).

acetic acid, and to the solution, maintained at a temperature of 50° and constantly stirred, 17 g. of bromine were gradually added. Fumes of hydrogen bromide were evolved. The mixture was allowed to stand for a short time, and then poured into four times its volume of cold water. The product was filtered at the pump, and washed with cold water. Yield, 26 g., or 84% of the theoretical.

3,3'-Diacetyl-amino-6,6'-dibromodiphenylmethane crystallizes in the form of small, colorless plates from glacial acetic acid, in which it is fairly soluble, or from alcohol, in which it is only slightly soluble. It is very difficultly soluble in ether, benzene, ligroin or carbon tetrachloride. The melting point is 284° .

0.2987 g. subs. required 27.1 cc. 0.05 *N* AgNO₃; 0.2964 g. gave 17.0 cc. N₂ (25° , 753 mm. over KOH).

Calc. for C₁₇H₁₆O₂N₂Br₂: Br, 36.34; N, 6.36; found: Br, 36.25%; N, 6.40%.

3,3'-Diamino-6,6'-dibromodiphenylmethane.—Sixty grams of the diacetyl compound and 250 cc. of alcohol were placed in a flask, provided with a reflux condenser. The mixture was heated to boiling, and then 200 cc. of hydrochloric acid (sp. gr. 1.19) were added gradually. After half an hour's heating saponification was complete, and the solution entirely clear. Soon the hydrochloride of the base began to crystallize out in the form of fine, colorless needles. At this point boiling was discontinued and the solution allowed to cool. The product was filtered off, and washed with alcohol, the greater part of the impurities remaining in the mother liquor. The latter was evaporated almost to dryness on the water bath, ammonia added, and the base extracted with ether. From the ethereal solution the almost pure salt was precipitated by means of hydrogen chloride.

When an aqueous solution of the hydrochloride is treated with ammonia the base is precipitated as an oil which soon solidifies to a mass of crystals, easily soluble in ether, alcohol or glacial acetic acid. After several recrystallizations from alcohol the substance showed a melting point of 114° . The base is rather unstable as, upon exposure to the air, it quickly turns brown.

On account of the instability of the free base it was decided to analyze the sulfate, since this salt was found to be only slightly soluble in cold water, and could easily be purified by recrystallization from this medium.

0.2983 g. subs. gave 14.1 cc. N₂ (20° , 746 mm.); 0.4602 g. subs. required 33.2 cc. 0.05 *N* AgNO₃.

Calc. for C₁₃H₁₂N₂Br₂.(H₂SO₄)₂: N, 5.07; Br, 29.02; found: N, 5.27; Br, 28.82.

A sample of the hydrochloride was titrated against standard potassium hydroxide solution, with phenolphthalein as indicator.

Calc. for C₁₃H₁₂N₂Br₂.2HCl: HCl, 17.40; found: 17.20.

2,2'-Dibromodiphenylmethane.—This substance was prepared by replacing in 3,3'-diamino-6,6'-dibromodiphenylmethane the amino groups

with hydrogen. Several unsuccessful attempts were made to eliminate the amino groups before a satisfactory method was found. Thus, neither the diazotization of the hydrochloride of the base by means of amyl nitrite in alcoholic solution, nor the reduction of the diazonium compound with sodium stannite, nor the oxidation of the corresponding hydrazine with copper sulfate or with potassium chromate led to satisfactory results. The procedure outlined below furnishes, however, a fairly good yield of 2,2'-dibromodiphenylmethane.

Ten grams of the hydrochloride of the base were made into a paste with 30 cc. of water and 10 cc. of hydrochloric acid (1.19). The mixture was maintained at a temperature of 0° while a cold, saturated solution of sodium nitrite was slowly added until a test with starch-iodide paper indicated free nitrous acid, the presence of a slight excess of which was found desirable since the salt diazotized somewhat slowly. When the mixture had become entirely homogeneous it was poured into one liter of boiling alcohol. A brisk evolution of nitrogen followed. The alcohol was distilled, and the remaining light brown oil taken up with ether. After the ethereal solution had been dried over calcium chloride, and the solvent removed, the residue was distilled under a pressure of 45 mm. The yield was 6.5 g. of a pale yellow, heavy liquid which came over between 220 and 245°. In an attempt to further purify the substance by distillation under 5 mm. pressure, a nearly colorless fraction was obtained between 212 and 218°. It seemed to be a mixture, however, and this supposition was confirmed by analysis.

0.2536 and 0.1403 g. subs. required 29.4 and 16.3 cc. 0.05 *N* AgNO₃.

Calc. for C₁₈H₁₀Br₂: Br, 49.04; found: 46.32 and 46.42.

Since the bromine content was low it was supposed that the impurity might be the ethoxy derivative which might have been formed as a by-product in the decomposition of the diazonium salt by the alcohol. Accordingly, 12 g. of the distillate were shaken with 40 cc. of concentrated sulfuric acid, and the insoluble portion which rose to the surface of the acid was separated, and distilled under 40 mm. A colorless liquid, boiling constantly at 234–235° was collected.

0.1419 g. subs. required 17.2 cc. 0.05 *N* AgNO₃.

Calc. for C₁₈H₁₀Br₂: Br, 49.04; found: 48.44.

The indices of refraction and dispersion were determined by means of an Abbé refractometer.

$n_D(20^\circ) = 1.6300$

$n_F - n_C(20^\circ) = 0.0213$

Specific gravity: $D_4^{20} = 1.6197$.

Action of Metals upon 2,2'-Dibromodiphenylmethane.—A solution of 10 g. of 2,2'-dibromodiphenylmethane in 150 cc. of anhydrous ether was treated with a slight excess of sodium wire, and the mixture allowed to

remain at room temperature for 24 hrs. After filtration and distillation of the ether, the original bromo compound was recovered unchanged.

Two grams of 2,2'-dibromodiphenylmethane and an excess of sodium wire were added to 50 cc. of anhydrous xylene, and the solution maintained at the boiling point for 6 hrs. Except for a slight reduction to diphenylmethane, due probably to a trace of moisture, there was no apparent action.

Two grams of the bromo compound, together with 2 g. of copper bronze, were heated to a temperature of 260° for several hours, according to the method of Ullmann. The original compound was recovered unchanged.

In the same manner, and with similar results, 2 g. of 2,2'-dibromodiphenylmethane with 2 g. of powdered magnesium and a trace of iodine were maintained at a temperature of 260° for one hour.

2,2'-Dibromodiphenylketone.—Five grams of 2,2'-dibromodiphenylmethane were dissolved in 50 cc. of glacial acetic acid. Ten grams of chromic anhydride in saturated aqueous solution were added, and the mixture heated on the water bath for six hours. The solution was then poured into ten times its volume of water, and the ketone extracted with ether. The acetic acid was removed from the ethereal extract by shaking with dilute potassium hydroxide solution. After drying over anhydrous sodium sulfate, and distillation of the ether, a colorless oil remained. A few cubic centimeters of alcohol were added to the oil, and the mixture stirred, whereupon the ketone was obtained as a crystalline mass. From its alcoholic solution the substance separates in the form of beautiful, hexagonal plates, melting at 86°.

2,2'-Dibromobenzophenone is insoluble in water; readily soluble in ether, acetone, chloroform, carbon tetrachloride, hot glacial acetic acid or hot alcohol.

0.3067 g. subs. required 35.6 cc. 0.05 *N* AgNO₃.

Calc. for C₁₃H₈OBr₂: Br, 47.02; found: 46.38.

In an attempt to prepare the oxime, equivalent quantities of ketone, hydroxylamine sulfate and potassium hydroxide in dilute alcoholic solution were heated for eight hours under a reflux condenser. Water was then added, and the mixture extracted with ether. From the ethereal solution the ketone was recovered unchanged.

In the same way, attempts to prepare the semicarbazone yielded negative results, even though the solution was allowed to stand for a month.

Oximes of analogously constituted ketones have never been prepared, owing probably to steric hindrance. Under very energetic treatment a Beckmann rearrangement may take place. If one of the substituents in the ortho position is a halogen atom another type of reaction may occur under the influence of alkali: formation of a five-membered heterocyclic compound of the isoxazole type.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

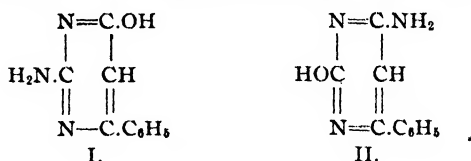
RESEARCHES ON PYRIMIDINES. LXXIV. SYNTHESIS OF
4-PHENYLCYTOSINE.

BY TREAT B. JOHNSON AND E. HEATON HEMINGWAY.

Received December 16, 1914.

Introduction.

In a previous publication from this laboratory entitled "The Isomerism of 4-Phenylisocytosine," Johnson and Hill¹ have given a description of four isomeric modifications of this aminopyrimidine. Each modification was characterized by its crystalline habit and also by the property of crystallizing in an anhydrous condition. All four isomers, however, combined with hydrochloric acid forming the same monohydrochloride which contained one molecule of water of crystallization. Nothing definite regarding the constitution of these four isomers was contributed. In continuing the study of this question of pyrimidine-isomerism it became of special interest to determine first whether other types of pyrimidines, besides those containing the guanidine grouping, would likewise undergo metameric changes. In other words, is this simply a special case of physical isomerism or a type of pyrimidine-stereoisomerism which theoretically might be expected to occur in other classes of pyrimidines. As a typical representative of another type of aminopyrimidines we, therefore, selected for investigation a urea combination; *viz.*, 4-phenylcytosine (II), whose relationship to 4-phenylisocytosine (I) is apparent by inspection of the two following formulas. Formula I represents a



guanidine compound while phenylcytosine (II) contains the amidine grouping $\text{H}_2\text{N}-\text{C}=\text{N}-$. A description of the synthesis and properties of this pyrimidine (II) is now given in this paper.

Phenylisocytosine (I) is prepared by the interaction of guanidine carbonate with ethyl benzoylacetate in alcohol solution. Jaeger² and Warmington³ independently prepared the pyrimidine in this manner and their observation was confirmed by Johnson and Hill.⁴ The latter also observed that isomeric modifications of this pyrimidine are obtained by condensing guanidine with the β -ketone ester in the presence of sodium ethylate.

¹ THIS JOURNAL, 36, 1202 (1914).² Ann., 262, 373 (1890).³ J. prakt. Chem., [2] 47, 214 (1893).⁴ Loc. cit.

By the condensation of thiourea with ethylbenzoylacetate, 2-thio-4-phenyluracil (III) is easily obtained. Warmington¹ accomplished this synthesis by heating dry thiourea or ammonium thiocyanate with the β -ketone ester at 170–180°, and obtained a yield of pyrimidine corresponding to about 30% of the theoretical. Attempts to bring about this condensation under other conditions were unsuccessful. For example, Warmington¹ writes as follows: "Weder durch die Einwirkung von Chlorwasserstoffsäure, Bromwasserstoffsäure oder Iodwasserstoffsäure oder von Natriumäthylat bei Gegenwart von Alkohol, noch durch die Verwendung von Eisessig als Lösungsmittel und nachheriges Einleiten von Salzsäuregas der Versetzen mit concentrirter Schwefelsäure in geringer Menge oder mit Essigsäureanhydrid gelang es, Benzoylessigester mit Harnstoff oder Thioharnstoff zu condensiren." On repeating Warmington's work we have not been able to confirm all his conclusions.

We now find that 2-thio-4-phenyluracil (III) can easily be prepared by digesting thiourea with ethyl benzoylacetate in alcohol solution and in the presence of sodium ethylate. In fact, the reaction is so smooth that a yield of the pyrimidine is obtained, which corresponds to over 73% of the theoretical. There is far less secondary decomposition than when the thiourea is heated directly with the β -ketone ester as recommended by Warmington.

2-Thio-4-phenyluracil (III) undergoes alkylation smoothly when its sodium salt is digested in alcohol solution with ethyl bromide, giving the corresponding mercaptopyrimidine, namely, 2-ethylmercapto-4-phenyl-6-oxypyrimidine (V). The corresponding 2-methylmercapto compound has been described by Wheeler and Merriam.² When digested with hydrochloric acid, mercaptan is evolved and the mercaptopyrimidine (V) is converted quantitatively into 4-phenyluracil³ (IV). 4-Phenyluracil is also quantitatively formed by direct desulfurization of 2-thio-4-phenyluracil (III). This is easily accomplished by digestion of the thiopyrimidine with chloroacetic acid.

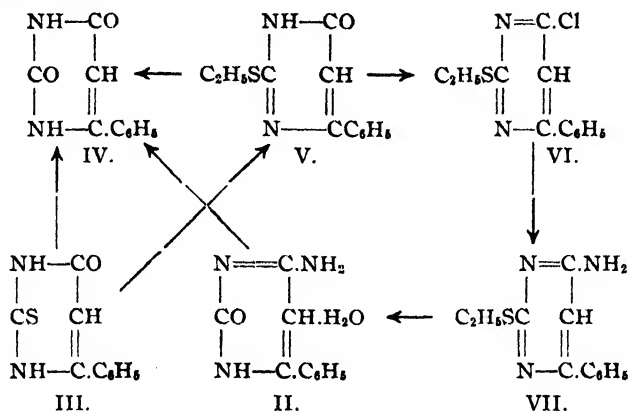
When 2-ethylmercapto-4-phenyl-6-oxypyrimidine (V) is warmed with phosphorus oxychloride they interact smoothly, forming the halogen derivative 2-ethylmercapto-4-phenyl-6-chloropyrimidine (VI). This chloropyrimidine can be distilled under reduced pressure without decomposition. If heated with strong alcoholic ammonia the halogen is removed and 2-ethylmercapto-4-phenyl-6-aminopyrimidine (VII) is the product of the reaction. This aminopyrimidine (VII) undergoes a normal hydrolysis when digested with hydrobromic acid solution, giving ethylmercaptan and the hydrobromic acid salt of 4-phenylcytosine. The yield of this

¹ *Loc. cit.*

² *Am. Chem. J.*, **29**, 478 (1903).

³ Warmington, *Loc. cit.*

salt is nearly quantitative. The free base (II) is easily obtained by decomposing this salt with the required amount of ammonia or sodium hydroxide. These various transformations are expressed by the following structural formulas:



While cytosine¹ crystallizes with one molecule of water, it is of interest to note that this is not a general property which is characteristic of its carbon-substituted derivatives. In fact, only one of the thirteen carbon-substitution products, thus far described in papers from this laboratory, has crystallized in a hydrous condition; *viz.*, 5-aminocytosine.² We now find that phenylcytosine is another exception to the rule and likewise crystallizes with one molecule of water. Phenylcytosine is not characterized by such unique physical and chemical properties as was observed in the case of its isomer phenylisocytosine.³ It does, however, exist in two distinct modifications. Neither modification possesses any definite melting or decomposition point. They are, however, characterized by their individual crystalline habit. Both modifications are obtained by crystallization from alcohol and also undergo interconversion in the same solvent. The conditions under which these changes are produced are described in the experimental part of this paper. Both modifications combine with hydrochloric and hydrobromic acids respectively, giving the same salts.

Experimental Part.

The ethylbenzoylacetate, which was used in this work, was prepared according to the directions of Wahl and Doll.⁴

2-Thio-4-Phenyluracil (III).—This pyrimidine can easily be prepared according to the following procedure: Three and three-tenths grams of

¹ Wheeler and Johnson, *Am. Chem. J.*, **29**, 492 (1903).

² Johnson, Johns and Heyl, *Ibid.*, **36**, 160 (1906).

³ Johnson and Hill, *Loc. cit.*

⁴ *Bull. soc. chim.*, [41] **13**, 265 (1913).

metallic sodium are first dissolved in 45 cc. of absolute alcohol and 7 g. of thiourea dissolved in the solution. Thirteen and eight-tenths grams of ethyl benzoylacetate are then added and the mixture digested on the steam bath for several hours (10-12). The excess of alcohol is then evaporated by heating at 100° and the sodium salt of phenylthiouracil dissolved in the least possible quantity of cold water. This solution is then cooled and acidified with hydrochloric acid when the pyrimidine will separate in a crystalline condition. The yield obtained was 10.7 g., corresponding to about 73.3% of the theoretical. It crystallized from acetic acid in needles and melted at 259°.

Desulfurization of 2-Thio-4-phenyluracil by Digestion with Chloroacetic Acid.—Four grams of the thiopyrimidine and 4 g. of chloroacetic acid in 12 cc. of water were digested on a sand bath. The thiopyrimidine dissolved and after digesting for 2 hours 4-phenyluracil began to deposit from the hot solution. On cooling, the desulfurized pyrimidine separated completely and was purified by crystallization from alcohol. It deposited as prismatic crystals which melted at 270°.¹ The yield was practically quantitative.

2-Ethylmercapto-4-phenyl-6-oxypyrimidine (V).—This mercaptopyrimidine is easily prepared by digesting the sodium salt of 2-thio-4-phenyluracil in alcohol solution with the required amount of ethylbromide. After the reaction is complete the alcohol is then removed by evaporation and the mercaptopyrimidine separated from sodium bromide by trituration with cold water. The pyrimidine is insoluble in this solvent. It can be purified best by crystallization from absolute alcohol. It separates from this solvent in the form of needles which melt at 226°. The compound is insoluble in ether but soluble in benzene. The yield was 78% of the theoretical. The compound was dried for analysis by heating at 120°.

Calculated for $C_{12}H_{12}ON_2S$, N = 12.06; found, N = 11.8.

2-Ethylmercapto-4-phenyl-6-chloropyrimidine (VI).—Our method of preparing this halogenated pyrimidine was as follows: Twenty-two and five-tenths grams of the mercaptopyrimidine were placed in a dry flask and the latter connected with a reflux condenser. One hundred cc. of phosphorus oxychloride were then added through the condenser tube and the mixture heated on a steam bath. Hydrochloric acid was copiously evolved and the pyrimidine completely dissolved. After 5 hours' digestion the excess of phosphorus oxychloride was then removed by heating at 40-45° under diminished pressure and the residue poured into about 300 cc. of cold water. After thorough agitation to decompose any phosphorus halides present, the pyrimidine was then extracted with ether. The ether solution was washed with dilute sodium hydroxide solution and finally dried over anhydrous calcium chloride. After removal of the ether

¹ Wheeler and Merriam, *Am. Chem. J.*, 29, 490 (1903).

the pyrimidine was then purified by distillation under diminished pressure. It practically all distilled at 232° at 26.5 mm. pressure and the oil showed no signs of solidifying when cooled to -10° . The yield of purified product was 19.5 g. or 80.6% of the theoretical. In a second experiment we used 13 g. of the mercaptopyrimidine and obtained 9.45 g. of the chloropyrimidine boiling from $235-245^{\circ}$ at 30-40 mm. pressure.

Calculated for $C_{12}H_{11}N_2SCl$, $N = 11.18$; found, $N = 11.03$ and 11.10 .

The chloropyrimidine is converted quantitatively into 4-phenyluracil by hydrolysis with hydrochloric acid.

2-Ethylmercapto-4-phenyl-6-aminopyrimidine (VII).—This aminopyrimidine is formed by heating the above chloropyrimidine with strong alcoholic ammonia for two hours at $130-135^{\circ}$. On opening the bomb tube there was no pressure, but ammonium chloride was suspended in the solution. This was separated by filtration and the solution evaporated at 100° when the aminopyrimidine was obtained as an oil which solidified on cooling. The yield was 15.5 g. It was further purified by crystallization from 9.5% alcohol. It crystallized from this solvent in thin plates which melted at 120° to a clear oil. In a second experiment we obtained 6 g. of pure aminopyrimidine from 9.4 g. of the chloropyrimidine.

Calc. for $C_{12}H_{13}N_3S$, $N = 18.18$; found, $N = 18.01$ and 18.25 .

4-Phenylcytosine (II).—This pyrimidine was obtained in the form of its hydrobromic acid salt by hydrolysis of 2-ethylmercapto-4-phenyl-6-aminopyrimidine with hydrobromic acid. Eleven grams of the mercaptopyrimidine were dissolved in 75 cc. of hydrobromic acid and the mixture boiled on a sand bath for 6 hours when the evolution of mercaptan had ceased. The hydrobromide separated on cooling. After evaporating the excess of acid the salt was then purified by crystallization from water. It separated in the form of long needles which did not melt below 300° . The salt contained one molecule of water of crystallization which was determined by heating at 110° . Nitrogen determination on anhydrous salt.

Calc. for $C_{10}H_{10}ON_3Br \cdot H_2O$, $N = 15.67$, $H_2O = 6.29$; found, $N = 15.85$ and 15.51 , $H_2O = 6.20$.

In order to obtain the free pyrimidine base (4-phenylcytosine) this salt was dissolved in water and the hydrobromic acid neutralized by adding aqueous ammonia solution. The pyrimidine separated at once in a crystalline condition. This base is insoluble in cold ammonia but soluble in sodium hydroxide solution. The pyrimidine dissolved in boiling water and alcohol and crystallized from both solvents in the form of needles arranged in rosets. They did not melt or decompose below 300° . When this base was first prepared (January, 1914), it was observed to crystallize only in the form of needles. This material was then bottled and not examined further until November, 1914. It had not changed in appearance during this time. On recrystallizing the pyrimidine from alco-

hol as before we observed, however, a remarkable difference in behavior. The compound dissolved without difficulty in boiling absolute alcohol, but, on cooling, needles did not deposit as previously observed. Instead, the pyrimidine separated in characteristic blocks of rhombohedral habit. If recrystallized from 95% alcohol a mixture of needles and blocks was obtained in which the blocks predominated. In fact it was almost impossible to obtain needles alone by crystallization from alcohol. The pyrimidine base was synthesized a second time in November, 1914, and purified according to our original method. The base behaved exactly as the original preparation. We could obtain at will, by crystallization from 95% alcohol, the needle and prism modifications. Although the pyrimidine was purified by crystallization from absolute and 95% alcohol it still contained one molecule of water of crystallization. So firmly was this bound in the molecule that it could not be expelled by heating at 100°. At 120° it was removed with difficulty. At the same time the pyrimidine apparently underwent a partial hydrolysis, which accounts for the low analytical values obtained for nitrogen.

Water determination:

Calc. for $C_{10}H_9N_3 \cdot H_2O$, $H_2O = 8.7$; found, $H_2O = 8.31$.

Nitrogen determinations in the anhydrous base:

Calc. for $C_{10}H_9ON_3$, $N = 22.4$; found, $N = 22.1, 21.91$ and 21.95 .

Hydrochloride, $C_{10}H_9ON_3 \cdot HCl \cdot H_2O$.—This salt is easily obtained by dissolving the pyrimidine base in dilute hydrochloric acid and then allowing the solution to crystallize. It separated in the form of long, colorless needles which melted at 274° with decomposition. The salt was dried for analysis over concentrated sulfuric acid.

Calc. for $C_{10}H_9ON_3 \cdot HCl \cdot H_2O$, $N = 17.44$; found, $N = 17.58$ and 17.49 .

The nitrate of 4-phenylcytosine is characterized by its property of crystallizing from water in two distinct forms. When it deposits from a hot, saturated aqueous solution it first separates in the form of needles. This form, however, is not permanent and as the solution cools the needles disappear and are replaced by characteristic prismatic crystals. The salt decomposes when heated above 245°.

NEW HAVEN, CONN.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON HYDANTOINS. XXX. STEREOISOMERIC MODIFICATIONS OF BENZALHYDANTOIN.

By TREAT B. JOHNSON AND JOSEPH S. BATES.

Received December 16, 1914.

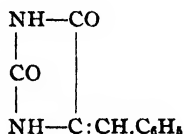
Benzalhydantoin (II) was first prepared by Ruhemann and Cunningham¹ by heating ethyl phenylpropiolate with urea in alcohol solution and in the

¹ *J. Chem. Soc.*, 75, 938 (1899).

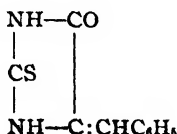
presence of sodium ethylate. They supposed the product of this reaction to be the ureide (I) and it was not until Ruhemann and Stapleton¹ later reinvestigated the reaction that it was shown that this conclusion was incorrect, and that the compound formed is really the hydantoin represented by Formula II. Thiourea and guanidine condense in an analogous manner, giving the corresponding cycles represented by Formulas III and IV, respectively.



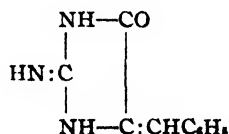
I.



II.



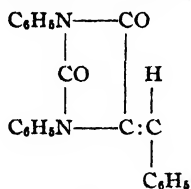
III.



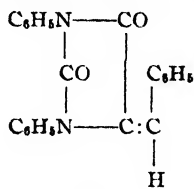
IV.

No attention was paid further to this hydantoin (II) until 1911 when Wheeler and Hoffmann² found that the same compound is obtained smoothly by condensing hydantoin with benzaldehyde. They assigned to the compound the same melting point as observed by Ruhemann and his co-workers, namely, 220°. Since this work of Wheeler and Hoffmann the hydantoin has been prepared a great many times by their method and in large quantities, but in no case has it hitherto been observed to melt otherwise than at the temperature mentioned.

Recently, Mr. Hadley, of this laboratory, has made the interesting observation that the aldehyde-condensation products of disubstituted hydantoins are capable of existing in isomeric modifications. For example, benzaldiphenylhydantoin (V and VI) occurs in two modifications³ which melt at 152° and 192°, respectively. One form, however, the higher melting, represented the chief product of the reaction. With this result



V.



VI.

in hand it immediately became of interest to examine more carefully the products of the reaction when hydantoin undergoes condensation with benzaldehyde. This has now been done and we have made the interesting observation that Ruhemann and Stapleton's *benzalhydantoin* (II) likewise occurs in two isomeric modifications. Both isomers are formed by con-

¹ *J. Chem. Soc.*, 77, 246 (1900).

² *Am. Chem. J.*, 45, 368 (1911).

³ Johnson and Hadley, *THIS JOURNAL*, 37, 171 (1914).

densing hydantoin with benzaldehyde. Ruhemann and Stapleton's¹ hydantoin melting at 220° is the chief product of the reaction as generally observed in our previous experiments.

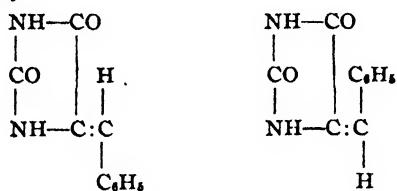
The isomeric modification (*trans*-benzalhydantoin) was identified in the alcoholic filtrates left after purification of the hydantoin melting at 220° (*cis*-benzalhydantoin). It deposited after concentration of these liquors, and was purified by a fractional crystallization from 95% alcohol. It separated from this solvent in burrs or aggregates of distorted prisms which melted at 246° to a clear oil. This modification is less soluble in alcohol than the isomer melting at 220°.

Calc. for $C_{10}H_8O_2N_2$, N = 14.89; found, N = 14.78.

The yield of this hydantoin melting at 246° is extremely small, being less than 1% of the theoretical. An attempt to prepare this modification by heating the isomer melting at 220° was unsuccessful. The latter was recovered unaltered after heating to the melting point of the higher modification (246°). In the case investigated by Johnson and Hadley¹ the higher melting modification of benzaldiphenylhydantoin (*trans*-form) was the chief product of the reaction. It is, therefore, a very interesting fact that benzaldehyde condenses with hydantoin in an anomalous manner, forming chiefly the lower melting modification of the hydantoin (*cis*-form melting at 220°).

Summary.

Benzalhydantoin (II) occurs in two modifications melting at 220° and 246°, respectively:



NEW HAVEN, CONN.

THE ACTION OF CHLORAL, BROMAL AND BENZALDEHYDE ON THE POLYCYCLIC HYDROCARBONS IN THE PRESENCE OF ALUMINIUM CHLORIDE.

[PART II.]

BY G. B. FRANKFORTER AND W. KRITCHEVSKY.

Received December 14, 1914.

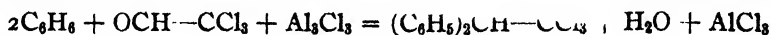
As has already been shown by us² when chloral is brought in contact with benzene or one of its derivatives in the presence of anhydrous aluminium chloride at the ordinary temperature, a violent reaction takes place,

¹ *Loc. cit.*

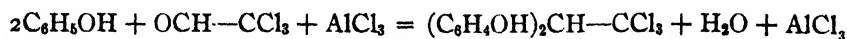
² *Bull.* 2, "Chemical Studies," University of Minnesota, also abstract, *THIS JOURNAL*, 26, 1511.

resulting in complete decomposition of both the chloral and the hydrocarbon; but when these substances are brought together at a low temperature, zero or below, an entirely different change takes place, resulting in most cases in a condensation reaction resembling very closely the so-called Baeyer reaction in which concentrated sulfuric acid is used as a condensation reagent.

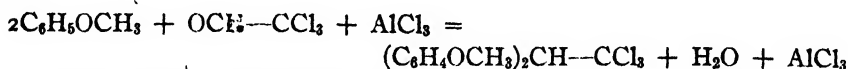
The aromatic compound in question is treated at 0° with chloral in the presence of aluminium chloride, and the following reaction takes place:



or



or



Condensation of Naphthalene with Chloral and Bromal by Means of Aluminium Chloride.—In order to determine whether or not the above condensation reaction could be extended to the more complex aromatic derivatives, experiments were begun on the polycyclic compounds. It was found, as will be shown in the following pages, that aluminium chloride acts in the same manner that it did with the aromatic compounds, forming analogous condensation products. The naphthalene reaction was unusually energetic; so much so, in fact, that great care was necessary in order to prevent total decomposition. In case the temperature was allowed to rise, decomposition began immediately; but if carefully controlled, at zero or below, the condensation reaction was almost quantitative.

α -Dinaphthyl-dichloroethylene, $(\text{C}_{10}\text{H}_7)_2\text{C}=\text{CCl}_2$.—One molecule of naphthalene and one of chloral were brought together and treated with one molecule of aluminium chloride for several hours, care being taken to keep the temperature at zero or below. After the reaction was completed, the mass was treated with water and finally distilled with steam. The black residue left was removed, extracted with ether and finally distilled *in vacuo*. Excess of naphthalene first sublimed in the condenser at 100° and 60 mm. pressure. The temperature then rapidly rose to 300° at 55 mm. pressure. At 160°, decomposition began with liberation of hydrochloric acid. Finally a thick red oil distilled over at about 300° which later crystallized on the cool walls of the condenser. The residue in the flask completely decomposed at 340°.

The red crystalline mass was removed from the condenser and examined. Treated with hot alcohol, the red color immediately disappeared and a part of the substance dissolved. The part insoluble in alcohol was found to be soluble in benzene. The alcohol-soluble part was crystallized several times from alcohol, when it appeared as transparent needles, m. p. 147–

148°. The molten crystals again took on the characteristic red color already observed in preparation. An examination indicated that the compound was doubtless α -dinaphthyldichloroethylene, the same compound which Grabosky prepared by an entirely different method. As α -dinaphthyltrichloroethane has a melting point of 150°, within but two degrees of the dichloro derivative, analyses were made with the following results:

Calc., C = 75.86, H = 4.02, Cl = 20.12; found, C = 75.80, H = 4.10, Cl = 20.02

The above analyses leave no doubt as to the compound being the ethylene derivative.

β -Dinaphthyldichloroethylene, $(C_{10}H_7)_2=C=CCl_2$.—The part in the above experiment which was found to be insoluble in alcohol was dissolved in benzene and allowed to evaporate when the substance crystallized out as white glistening crystals. The last traces of benzene and also traces of the α -compound were removed by washing with alcohol. The substance thus purified had a melting point of 219°. This substance also corresponds to the β -dinaphthyldichloroethylene which Grabosky prepared by an entirely different method.

β -Dinaphthyldibromoethylene, $(C_{10}H_7)_2=C=CBr_2$.—As has already been stated, when aluminium bromide is added to bromal in the presence of a hydrocarbon, no reaction takes place; but when aluminium chloride is substituted for the bromide, a vigorous reaction takes place, requiring a freezing temperature in order to prevent complete decomposition. Two molecules of naphthalene were treated with one and a half of bromal and one molecule of aluminium chloride added, care being taken to keep the temperature at 0°, as the reaction became violent liberating hydrochloric acid gas if the temperature was allowed to rise to 10°. After keeping the temperature at 0° for three days the reaction seemed to be complete. The whole mass was poured into water in order to remove the aluminium chloride and the excess of bromal. The residue was then subjected to steam distillation. The dark residue left after steam distillation was dissolved in ether and then washed with a little dilute caustic soda solution. The ether solution was then removed, the ether evaporated and the residue distilled *in vacuo*. The first part distilled over between 60° and 120° at 10 mm. pressure as a perfectly colorless liquid. It contained both bromal and naphthalene. Between 120° and 250° a small quantity of yellow oil passed over. It had a distinct phenol odor. Between 250° and 320° decomposition began with the liberation of hydrochloric acid, while a yellow liquid distilled over and solidified in the neck of the condenser. The residue left in the flask was completely decomposed at 320°.

The crystalline substance was removed from the condenser and treated with cold alcohol, in which it was found to be insoluble. It is slightly soluble in hot alcohol. The insoluble part from the hot alcohol was

recrystallized several times from benzene. The purified substance had a melting point of $223-225^{\circ}$.

Analyses gave the following:

Calc. for $(C_{10}H_7)_2=C=CBr_2$: C = 60.27, H = 3.31, Br = 36.53; found, C = 60.20, H = 3.31, Br = 36.83 and 36.66

The substance which dissolved in alcohol was found to be a gummy mass on evaporating off the alcohol.

The Action of Chloral on Anthracene in the Presence of Aluminium Chloride.—The fact that chloral condensation products were obtained from naphthalene and its derivatives by treating with aluminium chloride led to preliminary experiments along the same line with anthracene.

Dianthracenedichloroethylene, $(C_{14}H_9)_2=C=CCl_2$.—Following out the method already described, one molecule of anthracene was suspended in ten volumes of petroleum ether, cooled to 0° and treated with one and a quarter molecules of chloral and, under vigorous stirring, one molecule of aluminium chloride was added. The temperature was not allowed to rise above 10° during the reaction. After the chloride had been added, the stirring was continued for several hours and the temperature allowed to gradually rise to 20° . During the reaction large volumes of hydrogen chloride were evolved. After standing a day at room temperature the reaction seemed to be complete. The petroleum ether was distilled off and the residue treated with water in order to dissolve the chloride and the unchanged chloral. The black residue which remained was purified by steam distillation and treated with alcohol and ether in order to remove last traces of anthracene. The substance remaining was dissolved in benzene and precipitated out by means of alcohol. The precipitate thus obtained was a brownish yellow powder. It was found to be insoluble in acids and bases, slightly soluble in alcohol, ether and carbon disulfide but very soluble in chloroform, carbon tetrachloride and benzene. It refused to crystallize from any of the solvents. It did not have a sharp melting point but turned black and began to decompose at 340° . It was purified several times by dissolving in carbon tetrachloride and precipitating with alcohol and also by dissolving in benzene and precipitating with alcohol. From 40 g. of the impure substance, 25 g. were obtained in pure form by reprecipitation.

Calc. for $(C_{14}H_9)_2=C=CCl_2$, Cl = 15.84; found, Cl = 16.15, 16.18 and 16.45.

9,10-Anthracenedichloroethylene, $C_{14}H_8=C=CCl_2$.—It was found that when anthracene was treated with chloral and aluminium chloride in the presence of benzene, the reaction appeared to be different from the one already mentioned, in which petroleum ether was used as a solvent. Accordingly, one molecule of anthracene and five molecules of chloral were dissolved in ten times their volume of benzene and treated with one molecule of aluminium chloride at 0° . The reaction which took place resembled,

in some respects, the one in which petroleum ether was used as the solvent. The yellow powder obtained was found to be insoluble in the inorganic solvents, namely, the acids and bases; slightly soluble in alcohol and ether but very soluble in benzene, chloroform and carbon tetrachloride. It refused to crystallize and did not have a sharp melting point. It decomposed at a very high temperature. Analyses of the purified substance gave numbers which correspond to the formula given above.

Calc. for $C_{14}H_8=C'CCl_2$, C = 70.84, H = 2.95, Cl = 26.12; found, C = 70.74, H = 3.19, Cl = 26.37.

From the analysis given above, it is evident that condensation took place with one molecule of anthracene instead of two as observed in the case of benzene, naphthalene and their derivatives.

In order to determine the position in which the chloral molecule entered the anthracene molecule, the substance was suspended in glacial acetic acid and oxidized with chromium trioxide, using the proportions of the substance acetic acid and chromium trioxide ordinarily given for the oxidation of anthracene to anthraquinone. The powder remained unchanged and no anthraquinone derivatives were formed. It is evident therefore, that the chloral had entered the gamma positions, thus preventing the formation of anthraquinone derivative. Duplicate oxidation experiments were made with pure anthracene, when anthraquinone was readily obtained.

From the above experiments it was evident that the solvent had something to do with the way in which the reaction goes. In order to test out more fully the solvent influence on the reaction, the above experiments were repeated using carbon disulfide as the solvent, when a different compound was obtained.

9,10-Anthracenetrichloroethane, $C_{14}H_8=CH-CCl_2$.—One molecule of anthracene was suspended in ten times its volume of carbon disulfide and treated with one and a half molecules of chloral and one of aluminium chloride. The temperature was kept at 0° . A small amount of hydrochloric acid was liberated. At the end of five or six hours the reaction seemed to be complete. The substance was partially purified by steam distillation and by washing with alcohol. The residue was then treated with ether, in which it was found to be partially soluble. The soluble part was examined and found to be composed of two or more substances which could not be separated. The insoluble part was dissolved in benzene and precipitated by means of alcohol. Thus obtained, the substance appeared as a brown amorphous powder without a distinct melting point. Analyses of the substance indicated that it was not quite pure. The experiment was, therefore, repeated, modifying the process by removing all of the water-soluble substances before treating with alcohol and ether. By dissolving in benzene and precipitating with alcohol several times

it was obtained in pure form. Thus obtained, it was a yellowish brown powder insoluble in all the common solvents except benzene, chloroform, carbon tetrachloride and acetone. It is unchanged by boiling alcoholic potash, concentrated nitric acid and bromine.

Analyses gave the following:

Calc. for $C_{14}H_8=CH-CCl_3$, C = 62.55, H = 2.93, Cl = 34.53; found, C = 63.05, H = 2.76, Cl = 32.50

Complete combustion of the substance was very difficult, owing to the fact that some of the carbon was deposited on the porcelain boat as graphite. This unusual stability may be due to the fact that the chloral radical is joined to the anthracene in the meso position, as was also indicated by the oxidation experiments.

The Action of Bromal on Anthracene in the Presence of Aluminium Chloride and Carbon Disulfide.—Bromal readily reacts with anthracene in the presence of aluminium chloride, especially when carbon disulfide is used as a solvent. As has already been stated, no reaction takes place if aluminium bromide is used instead of the chloride. Furthermore, the temperature must be kept near 0° in order to obtain satisfactory results.

9,10-Anthracenetribromoethane, $C_{14}H_8=CH-CBr_3$.—One molecule of anthracene and two of bromal were dissolved in ten volumes of carbon disulfide and one molecule of aluminium chloride added piece-meal. A very small amount of hydrochloric acid was liberated during the reaction. After the reaction was completed, the whole mass was washed with water until all of the water-soluble substances had been removed. The disulfide solution was separated from the water, treated with alcohol and shaken, when the substance was precipitated as a dark brown powder. It was filtered off, washed with alcohol, dissolved in benzene and reprecipitated with alcohol. By redissolving in benzene and reprecipitating several times, the substance changed to a chocolate-brown powder which did not melt at 360° . It proved to be insoluble in the acids and bases and in alcohol and ether. It is readily soluble, however, in chloroform, carbon tetrachloride and benzene. It is not changed by the ordinary oxidizing reagents; neither is it changed by bromine or alcoholic potash.

Analysis of the purified substance gave the following:

Calc. for $C_{14}H_8=CH-CBr_3$, C = 43.54, H = 2.04, Br = 54.43; found, C = 42.14, H = 2.30, Br = 52.82

Like the anthracene derivatives already mentioned, this substance is characterized by its unusual stability. This characteristic doubtless throws some light on the structure of the molecule, for it at least eliminates the aldol reaction which was observed in connection with the benzene reaction. Furthermore, the fact that no anthraquinone could be obtained by oxidation leads to the belief that chloral is joined to carbon atoms 9 and 10 in the anthracene molecule.

The Action of Chloral on Phenanthrene in the Presence of Aluminium Chloride and Carbon Disulfide.—Chloral reacts readily with phenanthrene in the presence of aluminium chloride. Best results were obtained, however, when carbon disulfide was used as a solvent.

9,10-Phenanthrenetricloroethane, $C_{14}H_8=CH-CCl_3$.—One molecule of phenanthrene was dissolved in two molecules of chloral, ten volumes of carbon disulfide and one molecule of aluminium chloride added. The reaction was violent and a large amount of hydrochloric acid liberated even though the temperature was kept at 0° . After the reaction was completed and the whole mass purified by means of water, alcohol and ether, it was finally obtained in pure form by dissolving in benzene and reprecipitating several times by means of alcohol. The substance thus obtained was a yellow powder without a definite melting point, but decomposing at a high temperature.

Calc. for $C_{14}H_8=CH-CCl_3$, C = 62.55, H = 2.93, Cl = 34.53; found, C = 62.59, H = 2.96, Cl = 34.76.

It was found to be insoluble in all of the common solvents except chloroform, carbon tetrachloride and benzene. It remains unchanged by treating with concentrated nitric acid and the common oxidizing and reducing reagents. It is evident again that the chloral has attached itself to the phenanthrene molecule in the meso position.

The Action of Bromal on Phenanthrene in the Presence of Aluminium Chloride and Carbon Disulfide.—Bromal does not combine with phenanthrene in the presence of aluminium bromide; however, when the chloride is substituted for the bromide, a vigorous reaction takes place even though the temperature is kept at 0° .

9,10-Phenanthrenetribromoethane, $C_{14}H_8=CH-CBr_3$.—One molecule of phenanthrene was dissolved in two of bromal, ten volumes of carbon disulfide and one molecule of aluminium chloride added. A vigorous reaction began immediately and a large amount of hydrochloric acid was liberated. After the reaction was complete, the compound formed was purified with water and alcohol as previously stated and finally reprecipitated several times from benzene by the addition of alcohol. The compound thus obtained was a yellow powder like the one previously mentioned; neither could it be obtained from any of the solvents in crystalline form. Like the previous compound mentioned it is soluble only in chloroform, carbon tetrachloride and benzene. It does not change when heated at 300° .

Analyses of the purified substance gave the following:

Calc. for $C_{14}H_8=CH-CBr_3$, C = 43.54, H = 2.04, Br = 54.43; found, C = 43.89, H = 2.45, Br = 54.05.

Like its analogous compounds, it remains unchanged in the presence of the common oxidizing and reducing reagents.

The Action of Benzaldehyde on Phenanthrene in the Presence of Aluminium Chloride and Carbon Disulfide.—One molecule of phenanthrene was dissolved in one and a half of benzaldehyde and five volumes of carbon disulfide. One and a half molecules of aluminium chloride were then cautiously added. After the reaction was completed and the whole mass purified by means of water, alcohol and ether, it was further purified by dissolving in benzene and reprecipitating several times with alcohol. On adding about half of the necessary amount of alcohol to completely precipitate out the substance from the benzene, and filtering, the substance may be separated into two distinct compounds: the one precipitated out by the alcohol as a resin of unknown composition, and the other a brown powder obtained by evaporating off the alcohol and benzene.

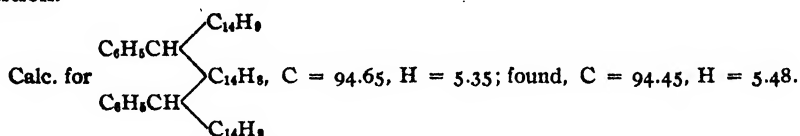
Diphenanthrenephenylmethane, $(C_{14}H_9)_2 : CH.C_6H_5$.—The above-mentioned brown powder was redissolved and reprecipitated several times by means of excess of alcohol. Analysis of the substance gave the following:

Calc. for $(C_{14}H_9)_2CHC_6H_5$, C = 94.59, H = 5.41; found, C = 94.19, H = 5.28

Molecular weight determination gave 445; calc. 444.

The purified substance was dark yellow powder melting and decomposing at 165° .

Dibenzalmesotriphenanthrene, $(C_6H_5CH)_2(C_{14}H_9)(C_{14}H_9)_2$.—The resinous substance above mentioned was purified several times by dissolving in benzene and reprecipitating by means of alcohol. The substance was finally obtained as a brown powder which melted at $195-197^\circ$ with decomposition.



Molecular weight determination gave 705; calc. 710.

We were unable to obtain any of these complex compounds in crystalline form. However, by reprecipitating several times as has already been indicated, they were from all appearances in pure form. It is unusual that these hydrocarbons, some of them at least, have a distinct color. Some of these colored substances are under investigation at the present time.

SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINNESOTA.

[FROM THE CHEMICAL LABORATORY, U. S. BUREAU OF MINES.]

THE SEPARATION OF THE CONSTITUENTS IN A NATURAL GAS FROM WHICH GASOLINE IS CONDENSED.

BY GEORGE A. BURRELL AND FRANK M. SEIBERT.

Received December 7, 1914.

In a previous communication¹ to THIS JOURNAL the authors showed

¹ THIS JOURNAL, 36, 1537 (1914).

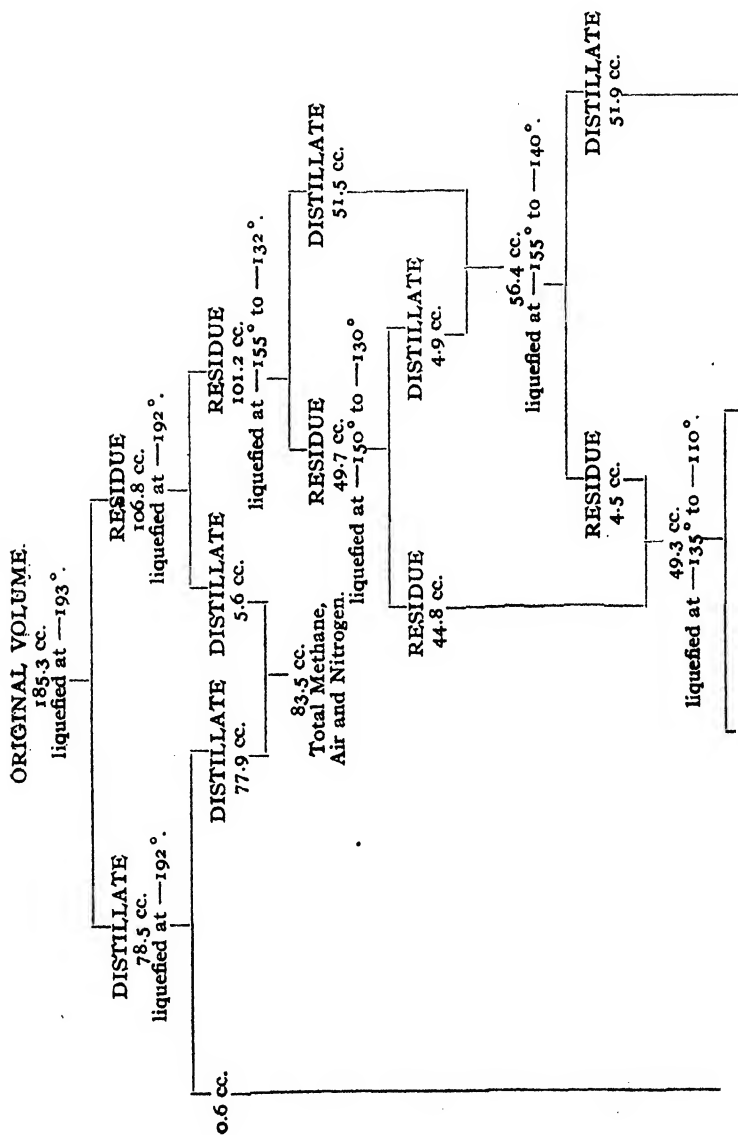
a method of separating the constituents in natural gas by fractional distillation in a vacuum at low temperatures. The gas experimented with was that used in Pittsburgh. Methane predominates in it with only small proportions of the higher paraffins. Not enough of the latter are present for the commercial condensation of gasoline. In this paper are shown the constituents in a natural gas that was obtained at a plant where the gas is treated for the condensation of gasoline. The procedure of separation is the same as that used in separating the constituents in the natural gas of Pittsburgh. Fig. 1 shows the various steps in the work. The original volume of the sample was 185.3 cc. At the temperature of liquid air 78.5 cc. of gas were removed, leaving a residue of 106.8 cc. Both the residue and distillate were reliquefied to obtain, as shown, by analysis pure methane mixed with air and nitrogen. This distillate amounted to 83.5 cc. Air had been accidentally introduced into the sample prior to the experiment. The final analysis was calculated air-free as given below to show the constituents originally present in the gas.

Second Series of Fractionations.—After the removal of the methane there remained a residue of 101.2 cc. containing ethane and higher paraffin hydrocarbons. This was liquefied and distilled and the distillate and residue from it liquefied and distilled again until finally at a temperature not higher than -140° there was obtained a distillate of 51.9 cc. that was pure ethane as nearly as could be determined by analysis. To this portion was added 0.6 cc. of ethane obtained in the first series of fractionations when the methane was separated. There resulted a total of 52.5 cc. ethane.

Third Series of Fractionations.—After the removal of the ethane there remained a total residue of 49.3 cc. consisting of propane and the higher paraffin hydrocarbons. The final fractionation in this series was made at a temperature not higher than -120° and resulted in obtaining 34.1 cc. of pure propane. It will be noted that the fractionations were carried to a point where only a small quantity (1.8 cc.) of propane was finally obtained.

Fourth Series of Fractionations.—After the removal of the propane there remained a residue of 15.2 cc. that contained the butanes and higher paraffin hydrocarbons. A separation of this residue into two portions was made by removing some gas with the pump at a temperature not higher than -95° . An analysis of the distillate was made, the result of which indicated butane chiefly. It is certain that some of the butanes remained in the residue and that the distillate of 9.3 cc. contained at least a small quantity of the pentanes, etc., hence it is better to simply call the 15.2 cc. residue butanes and higher paraffin hydrocarbons.

There follows the results of the fractionation analysis showing, under *A*, the paraffins in cubic centimeters, under *B*, the analysis in per cent. of the sample with air, and under *C*, the analysis calculated air-free. The



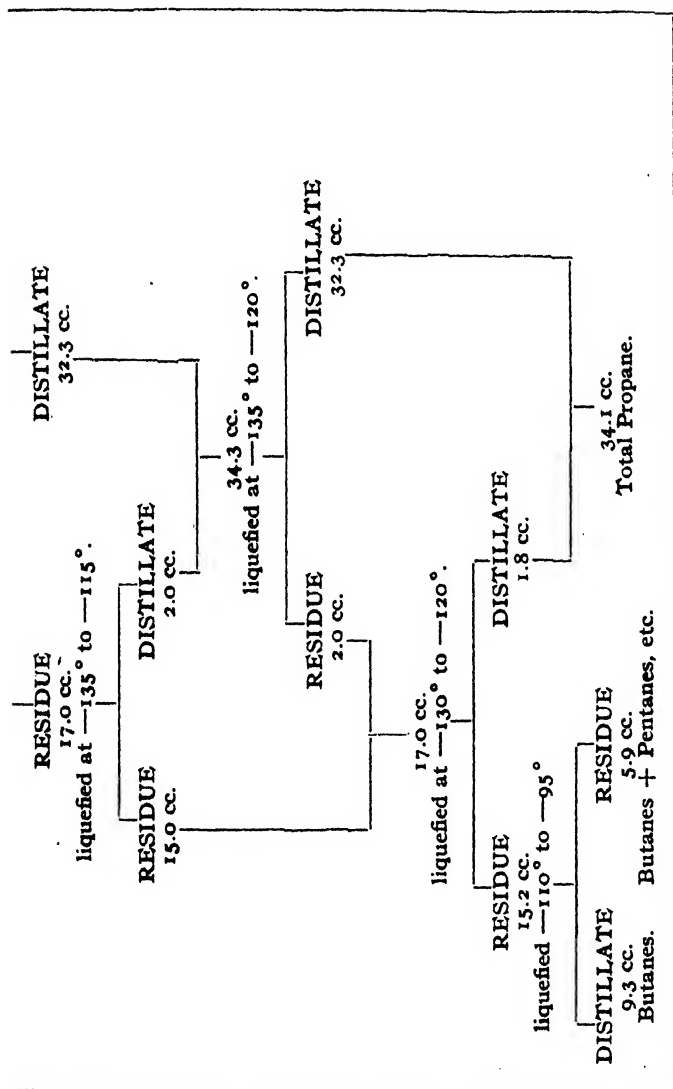


Fig. 1.—Fractionation analyses of natural gas.

air is foreign to the natural gas as it occurs in the wells and should, therefore, be eliminated. There is, however, about 1.0% nitrogen and about 0.03% carbon dioxide which are not shown in the analysis as presented.

FRACTIONATION OF NATURAL GAS FROM WHICH GASOLINE IS CONDENSED.

| | A. Cc. | B. Per cent. | C. Per cent. |
|---------------------------|-----------|-----------------|-----------------|
| Air + nitrogen..... | 24.5 | 13.2 | |
| Methane..... | 59.0 | 31.9 | 36.8 |
| Ethane..... | 52.5 | 28.3 | 32.6 |
| Propane..... | 34.1 | 18.4 | 21.1 |
| Butanes (chiefly)..... | 9.3 | 5.0 | 5.8 |
| Pentanes and hexanes..... | 5.9 | 3.2 | 3.7 |
| Total..... | 185.3 | 100.00 | 100.0 |

For comparison there is shown the fractionation analysis of the natural gas of Pittsburgh.

FRACTIONATION ANALYSIS OF THE NATURAL GAS OF PITTSBURGH.

| Constituents. | Per cent. |
|---------------------|------------------|
| Nitrogen..... | 1.6 ¹ |
| Methane..... | 84.7 |
| Ethane..... | 9.4 |
| Propane..... | 3.0 |
| Chiefly butane..... | 1.3 |
| Total..... | 100.0 |

Considerable difference will be noted between the quantity of the different paraffins in this gas mixture and in the one first described. The natural gas of Pittsburgh is used in immense quantities in the east for domestic and other purposes. The other represents a gas used for the condensation of gasoline. Temperatures are in degrees centigrade. Experimental details are shown in a previous communication.²

PITTSBURGH, PA.

EXPERIMENTS ON THE NATURE OF THE PHOTOGENIC SUBSTANCE IN THE FIREFLY.

By E. NEWTON HARVEY.

Received December 19, 1914.

Previous research on the subject of biophotogenesis has shown that at least three factors are necessary for the production of light, namely, water, oxygen and a photogenic substance. A fourth factor is probably also involved, an oxidizing enzyme, as in other organic oxidations. Concerning this enzyme nothing is known, at least nothing definite in the case of the firefly. Indeed Kastle's³ observations indicate that in the firefly

¹ Includes a trace of carbon dioxide, about 0.03%.

² *Loc. cit.*

³ J. H. Kastle, Hygienic Lab., Washington, D. C., *Bull.* 59, 92 (1910).

no direct oxidizing enzyme (oxygenase) but only small amounts of an indirect oxidizing enzyme (peroxidase) and a catalase are present.

The old observation that many luminous tissues can be dried and ground up and will phosphoresce, when water containing oxygen is again added, gives us a simple chemical method of investigating the nature of the photogenic material. The dried material may be extracted with water-free solvents (since the photogen does not oxidize in absence of water) and extracted material as well as the residue from evaporation of the filtrate tested for phosphorescence by adding water. Or, the dried material may be extracted with oxygen-free aqueous solvents (since the photogen does not oxidize with light production in absence of oxygen) and filtrate and residue tested as before by admitting oxygen. The first method is satisfactory and has indicated that a large number of fat solvents will extract nothing from the dried tissue and yet leave the photogenic material unharmed. Indeed, the material may be extracted with boiling ether for twenty-four hours without impairing its power to phosphoresce. Boiling alcohol does destroy the power to phosphoresce and the nature of its action is discussed below. These results, as well as the previous results of McDermott¹ and Dubois,² using fresh watery material, show conclusively that the photogenic substance is not a fat or fat-like body of any kind.

The second method—that of extraction with oxygen-free water solutions—is not satisfactory because the photogenic substance breaks up, or at least loses its power to phosphoresce, on standing in contact with water for any length of time *even if no oxygen is present*. Many attempts were made to extract the dried material with aqueous solvents and filter the extract in absence of oxygen before it was recognized that such attempts were futile because of the instability of the photogenic substance in oxygen-free water.

My experiments were begun in the winter of 1913 on firefly material collected at Princeton, N. J., and dried over CaCl_2 in a vacuum. (See preliminary note, Harvey.³) I am greatly indebted also to Mr. F. Alex. McDermott of the Mellon Institute, University of Pittsburgh, for an additional supply of material with which the work was continued. Mr. McDermott has been making experiments along similar lines with a somewhat different apparatus and his results are likewise published in this journal.⁴ As luminous material may be found which does not disintegrate in water the apparatus used for oxygen-free extraction is described below.

¹ F. A. McDermott, *THIS JOURNAL*, 33, 1791 (1911); *Smithsonian Report*, 1911, 345.

² *Orig. Comm. 8th Intern. Congr. Appl. Chem.*, 19, 86 (1912).

³ *Science*, 40, 33 (1914).

⁴ *Loc. cit.*

The material to be extracted is placed in the vessel C (Fig. 1), provided with a ground-in stopper connected with a 120° stopcock. The water to be rendered free of oxygen is placed in B after passing hydrogen through stopcock C and closing it. B is connected through A with a hydrogen

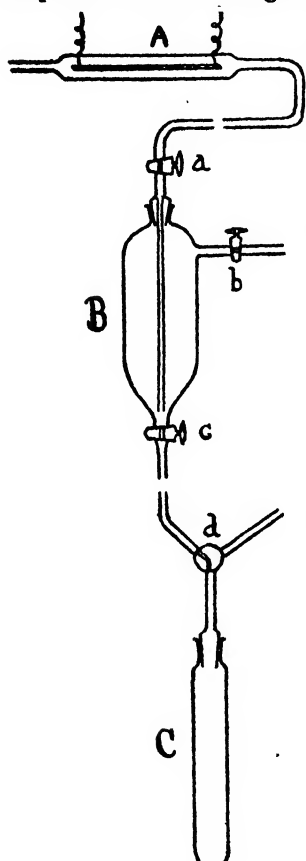


Fig. 1.

generator. The hydrogen is passed through potassium hydroxide to remove acid and then over a glowing platinum wire (in A) to remove the last traces of oxygen, a much better method than passing the gas through alkaline pyrogallol. By alternately exhausting B through *b*, connected to an air pump, and refilling with hydrogen several times the water can be quickly rendered free of oxygen. C is then connected to B through *c* and one of the arms of the 120° stopcock (*d*) whose other arm is connected with an air pump. C and the arms of *d* are then exhausted. The 120° stopcock is then turned to connect C and B and *c* is opened, allowing the pressure of the hydrogen to drive the solvent on the material in C. The proper amount of fluid for extraction should be placed in B so that the hydrogen may follow it through and fill the chamber C. Then *d* is closed, when C can be disconnected and shaken during extraction. To filter the extract it is only necessary to connect one of the arms of *d* with a desiccator fitted with funnel and filter rack. When the desiccator is exhausted, C and the desiccator are connected, and the pressure of the hydrogen in C drives the extract onto the filter paper. The firefly photogen begins to phosphoresce when the atmospheric pressure reaches 5–6 mm., which means an oxygen pressure of 1–1.2 mm. Consequently it is necessary to use a good vacuum pump and make connections air tight. I found that small bore lead tubing sealed with Khotinsky cement the best for the purpose.

If one extracts with distilled water for a short time (15 minutes) and then filters, on admitting oxygen the filtrate is found to be dark while the residue on the filter paper shows the bright points of light characteristic of the powder of the firefly. But if the extraction be carried out for an hour or more, neither the filtrate nor the residue will phosphoresce when oxygen is admitted. All of my experiments have been carried out in the dark and the material observed at critical stages (as when the oxygen-free water

was added) to make sure that no light appeared, and always with negative results. But to make sure that no very slow leakage of oxygen into the filtering chamber occurred, I have carried out the extraction in a special tube provided with a capillary sealed off during the extraction. After extracting in this tube for one and one-half hours and admitting oxygen no phosphorescence appeared. Thinking that possibly the photogen dissolved in the extracting fluid did phosphoresce, but only so faintly as to be invisible because distributed through a relatively large volume of extract fluid, the unfiltered extract was evaporated *in vacuo* to a small volume. This can be very easily done by placing the rubber tube from the vacuum pump over the capillary onto the special tube, exhausting, and then breaking the capillary through the walls of the rubber tube to connect with the air pump. Even when concentrated, the extract gave no light on adding oxygen.

The photogen is, therefore, destroyed in distilled water without oxidation. The search for a watery solvent for the photogen becomes then a search for a solvent in which the photogen is stable. The following solutions were tried in addition to distilled water. Extraction was allowed to proceed for from 1 to 1.5 hrs.

1. Ringer's solution (as representing fairly accurately the concentration and composition of the firefly's blood).

2. 0.125 *M* NaCl.

3. Sea water (a mixture of chlorides and sulfates of Na, K, Ca and Mg).

4. 5% NaCl.

5. 0.05 *M* NaOH and 0.01 *M* NaOH. The dried, powdered firefly organs will phosphoresce strongly if sprinkled on the surface of 0.1 *M* NaOH.

6. 0.02 *M* HCl. Dried firefly powder will phosphoresce on 0.0125 *M* HCl and on 0.025 *M* HCl, but less brilliantly. Only one or two bright dots appear on 0.05 *M* HCl and no phosphorescence occurs on 0.1 *M* HCl. If neutralized within two minutes after contact with the acid, the light does not appear in the 0.1 *M* HCl treated material nor become brighter in the 0.05 *M* and 0.025 *M* treated material.

In each case after extraction, oxygen was admitted and the solution shaken, yet in no case did light appear either in the undissolved residue or in the solution. The 0.02 *M* HCl extract was also neutralized as it is well known that the acid prevents biophotogenesis. The conditions of phosphorescence in the firefly are, therefore, more complex than at first supposed. Either the photogen, the enzymes, the enzyme activators or all three, undergo changes, which are not oxidative in nature, when the material stands in contact with water for a time sufficient to dissolve out the luminous material. Both McDermott's results and mine agree perfectly and while negative and disappointing they are deemed worthy of publication as indicating that water, oxygen and a photogenic

substance are not the only factors involved in light production and also as showing the instability of the photogen.

My work with water-free solvents has been confined to those listed in Table I, which gives also the time of extraction, temperature and results.

TABLE I.

| Substance. | Temperature. Degrees. | Time. Hrs. | Extracted material. | Extract evaporated in vacuo. |
|---|--------------------------|---------------|-------------------------|------------------------------------|
| Ether (cold)..... | 20 | 72 | + | — |
| Ether (hot)..... | 35 | 24 | + | — |
| Chloroform (cold)..... | 20 | 72 | + | — |
| Chloroform (hot)..... | 61 | 8 | + | — |
| Ethyl alcohol (cold)..... | 20 | 24 | + | — |
| Ethyl alcohol (hot)..... | 78.4 | 24 | — | — |
| Ethyl alcohol and ether (equal parts) boiling | 44 | 10 | + | — |
| Carbon tetrachloride..... | 20 | 48 | + | — |
| Carbon disulfide..... | 20 | 48 | — | — |
| Acetone..... | 20 | 48 | + | — |
| Toluol..... | 20 | 48 | + | — |
| Amyl alcohol..... | 20 | 48 | very faint ¹ | — |
| Ethyl butyrate..... | 20 | 48 | very faint ¹ | — |

A plus sign indicates phosphorescence when water is added and a minus sign indicates no phosphorescence. Both the original extracted material and the residue of the filtered extract evaporated to dryness were examined. The results indicate that the photogenic substance is not a fat or oil and also not a lecithin. I am aware that the lecithins are difficult to extract *in toto* from the cell, but this can be accomplished by a mixture of hot ether and alcohol, and yet a mixture of hot ether and alcohol will extract nothing which will phosphoresce from the firefly powder. We may safely say that the photogen is not a lecithin.

Of all the solvents tried only hot alcohol and cold amyl alcohol and ethyl butyrate gave results that would indicate a possible solution of the photogenic substance. And yet there is nothing in the filtrate residue that will phosphoresce when water or a neutralized 3% solution of H_2O_2 is added. Thinking that oxidizing enzymes might be necessary and that these had not been extracted by the fat solvents although the photogen had, the filtrate was also tested by adding a water extract of firefly organs, fresh or preserved with toluol or chloroform, and also by potato-juice which contains considerable quantities of oxidizing enzymes. In no case was phosphorescence observed. The boiling ethyl alcohol,² cold amyl alcohol, and ethyl butyrate must, therefore, break up the photogen. It is the alcohol itself and not the temperature (78.4°) of boiling alcohol which is

¹ The material was washed with ether to remove the amyl alcohol and ethyl butyrate.

² The 99.8% absolute alcohol was distilled over metallic calcium and collected in a receiver protected from the air by $CaCl_2$ in order to remove the last traces of water.

responsible for the destruction of the photogen as the dried powder will withstand this temperature for 24 hrs. without any appreciable diminution in its power to phosphoresce. McDermott finds that liquid sulfur dioxide and liquid ammonia also destroy the photogenic power.

The powder obtained by drying cultures of luminous bacteria behaves similarly to the firefly material.

These results indicate that it will be a vastly more difficult problem to isolate and identify the photogenic substance than might at first be supposed.

PRINCETON UNIVERSITY, PRINCETON, N. J.

EXPERIMENTS ON THE NATURE OF THE PHOTOGENIC PROCESSES IN THE LAMPYRIDAE.

By F. ALEX. McDERMOTT.

Received December 19, 1914.

During the summer of 1914, the writer made some tests along the same line as described in the preceding paper by Harvey (p. 396), and he also attempted to obtain evidence of the breaking down of nucleic acids during the photogenic process, as suggested by Lund.¹ While the results are mainly negative, they are of interest as confirming Harvey's experiences. The obvious limitations to such work, owing to the restricted amount of material available at one time, is a serious handicap to very extensive results. Most of the present writer's experiments were made on material prepared from *Photinus pyralis* and *P. castus*; some of the material from the former species had been collected at Washington, D. C., in the summer of 1911, and, after drying *in vacuo* over sulfuric acid, had been sealed *in vacuo* in small flasks. This latter material was very kindly supplied to me by Professor J. H. Kastle, Director of the Kentucky Agricultural Experiment Station. It was apparently as active as when first prepared.

Extractions were made in oxygen-free natural gas. After grinding, the tissue to be tested was placed in a small separatory funnel which had been filled with gas which had been passed through pyrogallol solution; the washed gas was allowed to pass through the funnel for some time to sweep out any air which may have entered when the tissue was placed in the funnel. For the filtering, a vacuum desiccator was fitted up with a small beaker, a wire funnel support and a small funnel with a folded filter. The desiccator was connected to the gas supply for some time in order to remove all the air. The solvent to be used was placed in a small Erlenmeyer flask provided with a tightly fitting stopper bearing two small bore stopcocks. The washed gas was passed through this flask for some time after the solvent had been run in, and the solvent was then heated

¹ Lund, *J. Exper. Zööl.*, 11, 415 (1911).

slowly to the boiling point, and kept boiling quietly for about a minute, *when it was allowed to cool slowly in a current of the gas (except in those cases in which it was used hot)*. When cool, both stopcocks were closed and the outgoing tube connected to the inlet of the separatory containing the material to be tested; both tubes were well blown out with the gas before connection, and kept surrounded by a current of gas while being connected; the outgoing stopcock on the flask and the ingoing on the separatory were then opened, then the ingoing stopcock on the solvent flask, and finally the outgoing on the separatory, the solvent being run into the separatory by the pressure of the gas, when the small flask was inverted. The stopcocks on the separatory were then closed and the solvent flask disconnected. The separatory was shaken thoroughly, so that the tissue would be fully exposed to the action of the solvent; in some experiments filtration was done immediately, while in other cases the tissue was allowed to stand in the solvent for some time, usually with occasional shaking.

Fifteen to twenty of the dried luminous segments, weighing about 0.05 to 0.07 g., were usually used in a test. The filtrate and residue were usually tested by first exposing to the air and then by adding hydrogen peroxide (3% solution) always in a dark room, the eyes being allowed to become accustomed to the darkness for at least ten minutes before applying the test. In no case was the emission of light from the filtrate observed, though in short, cold extractions with alkali some activity of the residual material was noticed—due to larger fragments of the material which had not been thoroughly penetrated by the solvent.

The following are some of the combinations which were used:

1. 15 organs; 25 cc. 0.15 N H_2SO_4 ; solvent used cold, and allowed to stand fifteen minutes after shaking before filtration: No light at any stage.
2. 15 organs; 20 cc. 0.03 N $NaOH$; solvent used cold, and allowed to stand fifteen minutes after shaking before filtration. No light on adding solvent to tissue; faint light on running liquid on filter: Filtration very slow; no light on testing residue and filtrate four hours later.
3. 15 organs; 20 cc. 0.05 N $NaOH$; solvent used cold and filtered immediately after shaking: No light at any stage.
4. 15 organs; 25 cc. 0.001 N $NaOH$; organs crushed rather than ground; solvent applied hot and filtered immediately after shaking: No light at any stage.
5. 4 repeated, using cold alkali; larger pieces of tissue glowed on treatment of residue with 3% H_2O_2 on filter; no light from fine material on the filter, nor from the filtrate. A very active catalase went into solution in the alkali in this experiment.

All the extracts had the characteristic odor of the insect, which was intensified by the alkali.

A considerable number of experiments were run using alkaline solutions as solvents, with the view that if nucleic acids were present, as suggested by Lund and were active in light production, they might be thus gotten into solution; in no case was an active extract obtained. To examine this

point further, determinations of the total nitrogen in the insects and in the luminous organs, and of the nitrogen, phosphoric acid and carbohydrates in the extracts were attempted. For the determination of the total nitrogen in the insects and in the luminous apparatus, dried specimens of *Photinus castus* collected in Pittsburgh, Pa., were used; this species is quite closely related to *P. pyralis* and it is unlikely that there would be any wide difference in the proportion or distribution of the nitrogen in them.

The mean of two determinations of the total nitrogen in the luminous tissue showed 13.6%, while the mean of two determinations on the remainder of the insect showed 10.3%; this would indicate about 11% N for the whole insect, calculated on the relative weights of the luminous segments and the remainder of the insect. All weights refer to the tissue dried *in vacuo* over sulfuric acid. The low figure for the total nitrogen of the insect is probably accounted for by the relatively large amount of chitin, while the high figure for the luminous tissue is undoubtedly due to the deposits of uric acid or closely related compounds which form the so-called reflecting layer, constituting the larger part of the bulk of the dry material from the luminous segments.

To test the possible effect of the photogenic processes on the amount of soluble nitrogen, phosphoric acid and carbohydrate, two experiments were run in parallel, using the tissue of *Photinus pyralis*. In the first test, (A), 0.146 g. of the ground dry tissue was treated with 20 cc. of hot 0.075 N H_2SO_4 , in natural gas; 1 cc. of 3% hydrogen peroxide and 20 cc. of water were then added, the mixture boiled and filtered and the filtrate and washings made up to 50 cc. In the second (B), 0.179 g. of the ground dry tissue was treated with 1 cc. of 3% hydrogen peroxide and 20 cc. of water in the air, and allowed to stand till the action and light-emission had ceased; 20 cc. of 0.075 N H_2SO_4 were then added and the solution boiled, filtered, and made up to 50 cc. By this means the material in the first test, (A), was kept from light production, while in the second test (B) the light-producing power was expended. The nitrogen was determined in 25 cc. portions of each of these filtrates, while a portion of the remainder was used for the titration of P_2O_5 with uranium acetate. Tests for optical activity were negative on both filtrates, which is taken to indicate the absence of significant quantities of carbohydrates. The results of the N and P_2O_5 determinations are given below:

| Test. | Per cent. of weight of dry tissue taken. | |
|--------|--|--|
| | N in solution, by Kjeldahl. | P_2O_5 in solution, by uranium acetate. |
| A..... | 4.81 | 0.515 |
| B..... | 4.14 | 0.420 |

These figures do not show as great a difference as might be expected were the photogenic process accompanied by any extensive breaking down

of nucleic acids, and the differences, indeed, are in the opposite direction to what would be expected under such circumstances.

From the evidence presented it is concluded that the deposits of purine substances which form the so-called reflecting layer of the photogenic organs of the Lampyridae cannot be traced satisfactorily to the breaking down of nucleic acids. In agreement with the work of Harvey, reported in the preceding paper, dilute acid and alkaline solutions, hot or cold, fail to extract a light-producing substance from the dry tissues of these insects, even when used in the entire absence of oxygen, and such solutions rapidly destroy the photogenic activity of the dry tissue.

MELLON INSTITUTE, UNIVERSITY OF PITTSBURGH,
PITTSBURGH, PA.

NEW BOOKS.

Qualitative Chemical Analysis. By CHALFANT E. BIVINS. New York: John Wiley and Sons. Price, \$1.00.

This manual is one of a series of loose-leaf laboratory manuals, edited by J. M. Jameson. The author has made no attempt to depart from conventional tests and separations. The book has, however, many excellent features. The directions are clear and easily followed; the discussion of procedures, explanatory notes, practice equations, and questions on the groups are excellent, and should be helpful to both teacher and student. The treatment of the analysis of alloys and metals is particularly good.

Comparatively little in the way of discussion of the principles of qualitative analysis has been attempted. The little that is given is so brief as to be of inconsiderable value. The statement that "*All the reactions of precipitation are ionic*, that is, are made by ions," would hardly be accepted even by many of the most ardent supporters of the theory of Electrolytic Dissociation. Likewise, the statement that "Oxidation is an increase in valence, and reduction a decrease in valence," leaves the student with an incorrect idea of these processes. No mention is made of the law of Mass Action and its applications.

For teachers who prefer to develop these subjects in the class room and wish a good laboratory guide, this laboratory manual can be used profitably.

JAMES H. WALTON, JR.

Food Products. By HENRY C. SHERMAN, PH.D. ix + 594 pp.; illustrated. New York: The Macmillan Company, 1914. Price, \$2.75.

During the last ten or fifteen years people have heard much about the origin and composition of foods and of laws to protect the purity of foods. Much of this discussion has been timely and it has acquainted the lay citizen with a class of facts which at one time appeared to be of interest to the food expert only. The lengthy papers and treatises on the somewhat

disagreeable topic of food adulteration have pretty thoroughly cleared the atmosphere over this field and have left as a desired result the assurance, that while there has been some adulteration in certain limited lines of food products, the extent of this has been far less than the rather lurid statements of overzealous writers would lead us to believe. Rational legislation has led to a pretty effectual check on the frauds which were attempted. The various discussions have led recently to the publication of several books which have the object of making different classes of readers acquainted with the essential facts regarding the production, control, and distribution of foods. The reviewer has had occasion to call attention to one of these, "The Source, Chemistry and Use of Food Products," by Professor Bailey, in a recent number of *THIS JOURNAL*. This book was intended primarily for students in certain grades of schools and colleges. The present book by Professor Sherman covers in a measure part of the same ground, but the discussion is such as to make it useful to a different group of readers.

Professor Sherman is the author of another work dealing with the subject of food as related to nutrition. In this book we are presented with another class of relations; the source of foods, the conditions of marketing, the purity of the products as they reach the consumer and the manufacture of canned or otherwise modified foods are treated in detail. The general character of the discussion makes the book more valuable to the chemist or food official than to the student or lay reader.

In different chapters practically the whole range of American foods is covered, and in a satisfactory manner. Appended to each chapter voluminous literature references are given and these seem full enough to satisfy the reader who may wish the original details of the discussions condensed in the text. Practically all that is recent and valuable in the literature of foods appears to be contained in these reference lists.

The second chapter deals with the subject of food legislation in a fair and non-partisan manner while in a long appendix the rules and regulations relating to the enforcement of the Food and Drugs Act are given in full, as are also the more important Food Inspection Decisions (F. I. D. bulletins) of the United States Department of Agriculture. The meat inspection laws and other laws are also given. Numerous tables throughout the book give the best-known results on the composition of various foods.

On the whole, the reviewer must express a very favorable opinion as to the scope and treatment of the material presented. J. H. LONG.

Methods of Quantitative Organic Analysis. By P. C. R. KINGSCOTT AND R. S. G. KNIGHT. New York: Longmans, Green and Co. 1914. xvi + 283 pp. Price, \$2.00 net.

The arrangement adopted in the book is based on a series of six lectures which the authors attended as students during the session of 1911-

1912 at the Imperial College of Science and Technology, London. In the first chapter is described the determination of molecular weights by physical methods; the ones considered are those of Victor Meyer, Bleier and Kohn, Dumas, Hofmann, and the cryoscopic methods as developed by Beckmann, Landsberger, and Walker. The second chapter deals with ultimate analysis. In addition to the methods of Liebig, Dennstedt, Dumas, Kjeldahl, and Carius, descriptions are given of the more recently described methods for the determination of oxygen, sulfur, halogens, phosphorus, arsenic, and antimony. The quantitative estimation of typical groups is considered in the third chapter; a large number of methods for determining the following groups are given: carboxyl, amino, substituted amino, imino, substituted imino, nitro, and carbonyl. The final chapter, which covers about one-half the pages in the book, is devoted to the description of processes for the quantitative determination of certain compounds of technical importance; these include carbohydrates, certain dyes, oils, fats, waxes, alkaloids, alcohols, phenols, acids, aldehydes, ketones, amines, chloroform, iodoform, chloral, ether, acetylenes, anthracene, vinegar, and wood-naphtha. Where such a wide field is covered it is evident that the treatment given to each topic must be very brief. In the case of most of the methods described, however, sufficient details are given to make it possible to carry out the method. It has, apparently, been the aim of the authors to include as many different processes as possible; for this reason the book is a valuable source of references to the literature.

JAMES F. NORRIS.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

TWENTY-SECOND ANNUAL REPORT OF COMMITTEE ON ATOMIC WEIGHTS. DETERMINATIONS PUB- LISHED DURING 1914.

By GREGORY PAUL BAXTER.

Received January 21, 1915.

During the past year reports of investigations upon many of the most used and important atomic weights have been published. The work upon carbon, sulfur, iodine, and the radio-elements, uranium and lead, is particularly interesting and significant.

Oxygen.—In the report for 1913 some gas density determinations by Scheuer¹ were overlooked. Oxygen was prepared from potassium permanganate and potassium chlorate, and after purification was fractionally distilled. The value obtained for the weight of the normal liter is a few units higher in the sixth figure than the one commonly assumed.

WEIGHT OF NORMAL LITER OF O₂.

| From KMnO ₄ . | | From KClO ₃ . | |
|--------------------------|---------|--------------------------|---------|
| 1.42908 | 1.42899 | 1.42889 | 1.42919 |
| 1.42888 | 1.42922 | 1.42904 | 1.42909 |
| 1.42924 | 1.42886 | 1.42921 | 1.42895 |
| 1.42911 | 1.42904 | 1.42898 | 1.42911 |
| 1.42913 | 1.42906 | 1.42909 | 1.42902 |
| 1.42889 | 1.42921 | 1.42897 | 1.42914 |
| Mean, 1.42906 | | Mean, 1.42906 | |

Mean, 1.42906

¹ *Anzeiger d. k. Akad. Wien*, 50, 378 (1913).

Nitrogen.—Scheuer also found the density of nitric oxide, using carefully purified gas.

WEIGHT OF NORMAL LITER OF NO.

| | | | |
|---------------|---------|---------|---------|
| 1.34002 | 1.34008 | 1.34019 | 1.34014 |
| 1.34028 | 1.34013 | 1.33994 | 1.34031 |
| 1.34022 | 1.34015 | 1.34021 | 1.34017 |
| 1.34004 | 1.34017 | 1.34023 | 1.33995 |
| Mean, 1.34014 | | | |

Computed by the method of limiting densities, N = 14.004.

Chlorine.—For hydrochloric acid Scheuer obtained the following results:

WEIGHT OF NORMAL LITER OF HCl.

| | | | |
|---------------|---------|---------|---------|
| 1.63925 | 1.63931 | 1.63910 | 1.63897 |
| 1.63894 | 1.63908 | 1.63929 | 1.63923 |
| 1.63912 | 1.63925 | 1.63918 | 1.63913 |
| 1.63915 | 1.63937 | 1.63915 | 1.63920 |
| Mean, 1.63917 | | | |

Computed by the method of limiting densities, HCl = 36.468 and Cl = 35.460.

Neon.—Leduc¹ fractionated neon with cocoanut charcoal at low² temperatures, and, using a 600 cc. globe, in two experiments found the gas to be 0.6964 and 0.6958 times as heavy as air at 0°. Allowance for a slight amount of impurity was made by taking the density as 0.695. From this value and the one 0.06948 for hydrogen, the atomic weight of neon is calculated to be 20.15 (H = 1.0075).

Carbon.—Timmermans² prepared propane (a) by the action of propyl iodide on "sodium ammonium" and (b) by the action of sodium on propyl cyanide. The gas was liquefied and fractionally distilled. The weights of the normal liter, found by the globe method, are given below:

| (a) | | | |
|-----------------|------------|------------|------------|
| Volume of globe | 564.88 cc. | 455.77 cc. | 351.91 cc. |
| | | | Mean. |
| | 2.02021 | 2.01928 | 2.01744 |
| | (2.02287) | 2.01807 | 2.01970 |
| | 2.02070 | 2.01940 | (2.02258) |
| | 2.01864 | 2.02110 | 2.02125 |
| | | | 2.02033 |
| Mean, | 2.01985 | 2.01946 | 2.01946 |
| | | | 2.01956 |
| (b) | | | |
| | 2.01809 | (2.01580) | 2.02127 |
| | 2.01807 | 2.02161 | 2.01947 |
| | 2.01928 | 2.01933 | (2.02352) |
| | | | 2.01930 |
| Mean, | 2.01848 | 2.02047 | 2.02037 |
| | | | 2.01957 |

General mean, 2.01956

¹ *Compt. rend.*, 158, 864 (1914).

² *Ibid.*, 158, 789 (1914).

The other data necessary for computing the molecular weight of propane are now being determined in Geneva.

Richards and Hoover¹ titrated weighed amounts of sodium carbonate, which had been fused in a current of dry carbon dioxide, against weighed amounts of a solution of hydrobromic acid which had been standardized both by titration against the purest silver and by weighing the silver bromide produced. The hydrobromic acid solution was found to be equivalent to 8.3113 g. in vacuum of silver bromide per 100.000 g. in vacuum of solution. Furthermore, the solution of sodium bromide resulting from the neutralization was compared with weighed amounts of silver. The weights in the table are corrected to the vacuum standard and the following atomic weights are assumed:

$$\text{Ag} = 107.880; \text{Br} = 79.916; \text{Na} = 22.995.$$

| Weight Na_2CO_3 . | Weight HBr solution. | At. wt. C. | Weight Ag. | At. wt. C. |
|-----------------------------------|----------------------|------------|------------|------------|
| 4.75555 | 202.744 | 12.008 | 9.68023 | 12.005 |
| 4.80081 | 204.673 | 12.009 | 9.77222 | 12.007 |
| 4.88936 | 208.457 | 12.004 | 9.95301 | 12.001 |
| 5.63157 | 240.119 | 11.997 | 11.46316 | 12.008 |
| 4.49516 | 191.646 | 12.006 | 9.15003 | 12.007 |
| 4.86256 | 207.307 | 12.008 | 9.89811 | 12.004 |

Mean, 12.005

Mean, 12.005

Sulfur.—Richards and Hoover² also neutralized weighed amounts of sodium carbonate with dilute sulfuric acid. The solution was evaporated to small bulk and transferred to a weighed quartz flask, and after evaporation of the solution to dryness the residual sodium sulfate was fused. Vacuum weights are given and the atomic weights of carbon and sodium are assumed to be 12.005 and 22.995, respectively.

| Weight Na_2CO_3 . | Weight Na_2SO_4 . | At. wt. S. |
|-----------------------------------|-----------------------------------|------------|
| 5.25191 | 7.03829 | 32.058 |
| 4.50977 | 6.04382 | 32.060 |
| 5.04233 | 6.75737 | 32.057 |
| 3.67340 | 4.92304 | 32.063 |
| 4.18724 | 5.61151 | 32.059 |
| 4.55100 | 6.09916 | 32.062 |

Mean, 32.060

Silver.—Richards and Cox³ have published further details of their experiments which show that lithium perchlorate, as prepared by Richards and Willard in their work upon the atomic weights of lithium and silver, is free from moisture. The question as to whether the atomic weight of silver is as low as 107.87 certainly is still an open one.

¹ THIS JOURNAL, 37, 95 (1915).

² *Ibid.*, 37, 108 (1915).

³ *Ibid.*, 36, 819 (1914).

Iodine.—Bates and Vinal¹ made a very careful comparison of the silver and iodine coulometers, using them in series. The silver coulometers were of Smith's "new type" and the "porous pot" varieties; the iodine coulometers of the form devised by Washburn and Bates, the iodine set free being titrated by means of an arsenite solution which had been standardized with weighed amounts of iodine. In the following tables each weight is the mean from several coulometers run in series. Vacuum corrections are applied to the weights of iodine and presumably to the weights of silver. $\text{Ag} = 107.880$.

| Weight silver. | Weight iodine. | At. wt. I. |
|----------------|----------------|------------|
| (4.10582) | (4.82959) | (126.897) |
| (4.10469) | (4.82862) | (126.907) |
| 4.09903 | 4.82224 | 126.914 |
| 4.39711 | 5.17273 | 126.910 |
| 4.10523 | 4.82851 | 126.887 |
| 4.12310 | 4.84942 | 126.884 |
| 4.10475 | 4.82860 | 126.904 |
| 4.18424 | 4.92130 | 126.883 |
| 4.10027 | 4.82247 | 126.882 |
| 4.10516 | 4.82844 | 126.887 |

Mean of last eight experiments, 126.894

Bates and Vinal point out that this result is subject to correction for inclusions of electrolyte by the silver deposits. While Rosa, Vinal and McDaniel² have recently expressed the opinion that highly crystalline deposits from the purest silver nitrate solutions do not contain significant inclusions, Richards and Anderegg³ have found the inclusions of electrolyte to amount to from 0.004 to 0.035% of the weight of silver, according to conditions. These proportions are somewhat larger than those recently found by Hulett. Richards and Anderegg point out that all atomic weights determined electrolytically in the past by comparison with silver coulometers are therefore in error, by amounts impossible of accurate estimation because of the irregular nature of the inclusions. If, however, an average correction, as found by Richards and Anderegg, of 0.015% is applied to Bates and Vinal's results, the atomic weight of iodine becomes 126.913, a value in much better agreement with the most recent gravimetric determination by Baxter, 126.932.

Guichard⁴ also has compared the atomic weight of iodine directly with that of oxygen by decomposing known weights of iodine pentoxide and weighing the products. The iodine pentoxide was prepared from iodic acid and was dried at 240° in a vacuum, the iodine was condensed in the decomposition apparatus and weighed, the oxygen was collected and weighed

¹ THIS JOURNAL, 36, 916 (1914); Bureau of Standards, *Sci. Paper* No. 218.

² Bureau of Standards, *Sci. Paper* No. 220 (1914).

³ THIS JOURNAL, 37, 7 (1915).

⁴ *Compt. rend.*, 159, 185 (1914).

as copper oxide. The various substances were all weighed in exhausted vessels against counterpoises, with the following results:

| Weight I_2O_5 . | Weight I_2 . | Weight O_2 . | Weight I_2 + weight O_2 . | Difference. |
|---------------------------------|-----------------------|-----------------------|---|-------------|
| 5.18051 | 3.93910 | 1.24183 | 5.18093 | —0.00042 |
| 7.80826 | 5.93688 | 1.87138 | 7.80826 | 0.00000 |
| 9.33281 | 7.09689 | 2.23637 | 9.33326 | —0.00045 |
| 6.23324 | 4.73922 | 1.49333 | 6.23255 | +0.00069 |
| 7.08076 | 5.38441 | 1.69714 | 7.08155 | —0.00079 |

The atomic weight of iodine is computed in three ways.

| $40 \frac{\text{wt. I}_2}{\text{wt. O}_2}$ | $40 \frac{\text{wt. I}_2}{\text{wt. I}_2\text{O}_5 - \text{wt. I}_2}$ | $40 \frac{\text{wt. I}_2\text{O}_5 - \text{wt. O}_2}{\text{wt. O}_2}$ |
|--|---|---|
| 126.88 | 126.92 | 126.87 |
| 126.90 | 126.90 | 126.90 |
| 126.94 | 126.96 | 126.93 |
| 126.94 | 126.89 | 126.96 |
| 126.91 | 126.96 | 126.89 |
| Mean, 126.91 | Mean, 126.93 | Mean, 126.91 |
| | General mean, 126.92 | |

No correction is made for moisture retained by the iodine pentoxide. It is noteworthy that the average deficiency of the weights of the products is 0.0028%, a quantity in close agreement with the moisture content of iodine pentoxide dried at the same temperature, as found by Baxter and Tilley,¹ 0.0023%. The second mean is raised, the third lowered by applying this correction. The general mean is not appreciably affected, however.

Guye and Germann² investigated iodine and silver for occluded gases. One gram of iodine was found to contain 0.000013 g. air. One gram of silver, which had been fused in a current of hydrogen, yielded 0.000034 g. carbon monoxide and 0.000008 g. moisture. Neither material was of the highest purity.

Barium.—De Coninck³ determined the proportion of carbon dioxide in barium carbonate by dissolving the salt in acid. The average of five experiments gave $\text{Ba} = 137.4$.

Nickel.—De Coninck with Gerard⁴ also has determined the atomic weight of nickel, by reducing the hydrated oxalate in a current of hydrogen.

| Weight $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. | Weight Ni. | At. wt. Ni. |
|---|------------|-------------|
| 0.4300 | 0.1380 | 58.60 |
| 0.4730 | 0.1517 | 58.54 |
| 0.3440 | 0.1104 | 58.60 |
| 0.3869 | 0.1241 | 58.55 |
| 0.5161 | 0.1656 | 58.58 |

Mean, 58.57

¹ THIS JOURNAL, 31, 212 (1909).

² *Compt. rend.*, 159, 225 (1914).

³ *Rev. gén. chim.*, 16, 245 (1914).

⁴ *Compt. rend.*, 158, 1345 (1914).

Cadmium.—Baxter and Hartmann¹ have determined the cadmium content of fused cadmium chloride by direct electrolysis with a mercury cathode.

| Weight CdCl ₂ . | Weight Cd. | At. wt. Cd. |
|----------------------------|------------|-------------|
| Preliminary Series. | | |
| 6.08570 | 3.73181 | 112.426 |
| 4.20489 | 2.57863 | 112.443 |
| 5.36203 | 3.28817 | 112.436 |
| 7.50512 | 4.60221 | 112.426 |
| 6.71591 | 4.11839 | 112.435 |
| 5.91556 | 3.62763 | 112.438 |
| 5.49323 | 3.36805 | 112.387 |
| 3.14416 | 1.92791 | 112.408 |
| 7.58705 | 4.65173 | 112.381 |
| 2.26738 | 1.39006 | 112.359 |
| 5.93501 | 3.63962 | 112.443 |
| 6.04122 | 3.70490 | 112.454 |
| 4.07400 | 2.49821 | 112.425 |

Mean, 112.420.

| | | |
|---------------|---------|---------|
| Final Series. | | |
| 9.00004 | 5.51879 | 112.419 |
| 6.56891 | 4.02808 | 112.423 |
| 7.12956 | 4.37174 | 112.414 |
| 8.57291 | 5.25679 | 112.415 |
| 7.76294 | 4.76011 | 112.413 |

Mean, 112.417

This result is considerably higher than the value recently found by Hulett and his collaborators, but in close agreement with that previously obtained by Baxter, Hines and Frevert.

Mercury.—H. B. Baker and Watson² synthesized mercuric bromide from the elements. An excess of bromine retained by the halide was quantitatively estimated. Vacuum weights are given in the table. Br = 79.92.

| Weight Hg. | Weight HgBr ₂ . | At. wt. Hg. |
|------------|----------------------------|-------------|
| 4.88190 | 8.77274 | 200.56 |
| 6.74796 | 12.12646 | 200.54 |
| 4.79430 | 8.61640 | 200.50 |
| 4.52480 | 8.13048 | 200.58 |
| 4.78892 | 8.60534 | 200.57 |
| 5.52880 | 9.93406 | 200.61 |
| 4.40148 | 7.90886 | 200.59 |
| 4.52338 | 8.12794 | 200.58 |
| 5.44704 | 9.78683 | 200.62 |

Mean, 200.57

¹ THIS JOURNAL, 37, 113 (1915).

² J. Chem. Soc., 105, 2530 (1914).

This value is 0.2 unit higher than the result reported a year ago by Taylor and Hulett, but confirms very closely the recent work of Easley.

Vanadium.—Briscoe and Little¹ synthesized vanadyl chloride from chloride and vanadium trioxide, and separated the product into four portions, A, B, C, D, by fractional distillation, with rejection of the two extreme fractions. Two of the four main fractions, C and D, were further fractionated in the same way into weighed bulbs which were sealed while exhausted. Analysis was effected by decomposition with ammonia, acidification, and comparison with silver. In two cases the silver chloride was collected and weighed. Vacuum corrections are applied. Ag = 107.880; Cl = 35.457.

| Fraction. | Weight VOCl ₃ . | Weight Ag. | At. wt. V. |
|-----------|----------------------------|------------|------------|
| C 2..... | 3.98162 | 7.43451 | 50.957 |
| C 3..... | 5.63804 | 10.52736 | 50.958 |
| C 5..... | 3.70889 | 6.92632 | 50.931 |
| C 6..... | 3.88228 | 7.24884 | 50.962 |
| D 1..... | 3.28485 | 6.13377 | 50.950 |
| D 2..... | 3.45920 | 6.45900 | 50.959 |
| D 5..... | 3.17088 | 5.92089 | 50.951 |
| D 6..... | 3.63990 | 6.79670 | 50.951 |
| D 7..... | 3.23254 | 6.20682 | 50.927 |

Mean, 50.950

| Fraction. | Weight VOCl ₃ . | Weight AgCl. | At. wt. V. |
|-----------|----------------------------|--------------|------------|
| C 4..... | 4.42279 | 10.97187 | 50.968 |
| D 8..... | 2.62557 | 6.51459 | 50.936 |

Mean, 50.952

This result agrees closely with the value recently found by McAdam, 50.96.

Tellurium.—Still another attempt has been made to separate from tellurium a related element of higher atomic weight. Dennis and Anderson² prepared hydrogen telluride from aluminum telluride by the action of dilute hydrochloric acid, and, after being dried, the gas was condensed with liquid air and fractionally distilled. Each fraction was converted to metallic tellurium at a high temperature, and, after being weighed, was oxidized with nitric acid and the dioxide was weighed. The results varied irregularly, 31 out of 45 falling between 127.3 and 127.8. Another specimen of hydride resulted from the electrolysis of a phosphoric acid solution with tellurium cathodes. The fractions of this preparation were caught in nitric acid and after being weighed as the dioxide were dissolved and titrated with potassium permanganate. The average of thirty-seven results, from 22 fractions, between 127.76 and 127.36, is 127.50. The authors consider that there is no evidence of the existence of divi-tellurium.

¹ *J. Chem. Soc.*, 105, 1310 (1914).

² *THIS JOURNAL*, 36, 882 (1914).

Radioactive Lead.—Four determinations of the atomic weight of radioactive lead appeared within a short period. Richards and Lambert¹ analyzed lead chloride obtained from minerals consisting largely of radioactive substances. The radioactivity due to β -rays was found several weeks after crystallization.

| Source. | Radioactivity referred to UO_2 . | Wt. PbCl_2 . | Wt. Ag. | Wt. AgCl . | At. wt. |
|----------------------------------|--|-----------------------|---------|---------------------|---------|
| Colorado carnotite..... | 21.8 | 3.87082 | 3.00984 | | 206.56 |
| | | 5.57331 | 4.33300 | | 206.60 |
| | | 5.49412 | 4.27157 | | 206.59 |
| | | 3.87082 | | 3.99879 | 206.59 |
| | | 5.57331 | | 5.75707 | 206.61 |
| | | 5.49412 | | 5.67573 | 206.58 |
| | | | | Mean, | 206.59 |
| Ceylon thorianite (Boltwood) 5.0 | | 3.88228 | 3.01600 | | 206.81 |
| | | 4.05550 | 3.15061 | | 206.81 |
| | | 4.05168 | 3.14788 | | 206.79 |
| | | 3.88228 | | 4.00703 | 206.84 |
| | | 4.05168 | | 4.18265 | 206.78 |
| | | | | Mean, | 206.81 |
| Ceylon thorianite (Miner).. | 3.8 | 2.80814 | 2.18162 | | 206.81 |
| | | 2.80814 | | 2.89816 | 206.85 |
| | | | | Mean, | 206.83 |
| Joachimsthal pitchblende.... | 5.7 | 3.95052 | 3.07209 | | 206.54 |
| | | 2.95726 | 2.29951 | | 206.56 |
| | | 2.95726 | | 3.05475 | 206.61 |
| | | | | Mean, | 206.57 |
| English pitchblende..... | 3.5 | 4.05702 | 3.15153 | | 206.84 |
| | | 4.05702 | | 4.18670 | 206.88 |
| | | | | Mean, | 206.86 |
| No. Carolina uraninite..... | 13.2 | 2.01795 | 1.56952 | | 206.47 |
| | | 2.01795 | | 2.08663 | 206.32 |
| | | | | Mean, | 206.36 |

By the same method Richards and Lambert found in preliminary experiments the atomic weight of common lead to be 207.15.²

Lead from Colorado carnotite was found to give a spectrum exactly like that of ordinary lead so far as could be determined.

¹ THIS JOURNAL, 36, 1329 (1914).

² Baxter and Grover have recently obtained the value 207.20 by analysis of both bromide and chloride. *Carnegie Institution Yearbook* No. 13. The details of this work will be published shortly.

Hönigschmid and Mme. Horowitz¹ utilized lead separated from pitchblende, and employed the usual chloride method. Their average result is between those of the two pitchblende samples examined by Richards and Lambert.

| Wt. PbCl ₂ . | Wt. AgCl. | Wt. Ag. | At. wt. |
|-------------------------|-----------|---------|---------|
| 1.97691 | 2.04118 | | 206.733 |
| 3.04040 | 3.13910 | | 206.746 |
| 3.05981 | 3.15939 | | 206.724 |
| 3.30285 | 3.41015 | | 206.740 |
| 3.33164 | 3.44013 | | 206.719 |
| 3.22459 | 3.32923 | | 206.749 |
| 3.33164 | | 2.58888 | 206.748 |
| 3.22459 | | 2.50586 | 206.730 |
| 3.79447 | | 2.71545 | 206.744 |

Mean, 206.735

M. Curie² also examined active lead from various minerals. After elaborate purification the metal was fused under cyanide and weighed. Then it was dissolved in nitric acid in quartz and the nitrate was dried at 150° before being weighed.

| Source. | At. wt. | At. wt. after repurification. | Mean. |
|----------------------|---------|-------------------------------|--------|
| Pitchblende..... | 206.60 | 206.68 | 206.64 |
| Carnotite..... | 206.38 | 206.34 | 206.36 |
| Yttriotantalite..... | 206.49 | { 206.59 206.55 | 206.54 |
| Monazite..... | 207.06 | 207.10 | 207.08 |
| Galena..... | 206.98 | 207.04 | 207.01 |

The results for pitchblende and carnotite, when allowance is made for the fact that ordinary lead from galena gave a low value, agree very well with those of Richards and Lambert, and Hönigschmid. It is noteworthy that monazite lead seems to possess a *higher* atomic weight than ordinary lead.

Soddy and Hyman³ by a comparative method also found lead from thorite to have an atomic weight 1.3 units *higher* than that of ordinary lead.

Fayans⁴ has discussed the bearing of Richards and Lambert's results upon the present theories of the relation of lead to radioactive disintegration.

Uranium.—Hönigschmid⁵ has analyzed uranium tetrabromide made by the action of bromine upon a mixture of the dioxide and carbon. In Series I the salt was sublimed, fused and allowed to solidify in an atmosphere containing bromine vapor; in Series II the salt was finally fused

¹ *Z. Elekt.*, 20, 319, 457 (1914); *Compt. rend.*, 158, 1796.

² *Compt. rend.*, 158, 1676 (1914).

³ *J. Chem. Soc.*, 105, 1402 (1914).

⁴ *Z. Elekt.*, 20, 449 (1914).

⁵ *Ibid.*, 20, 452 (1914); *Compt. rend.*, 158, 2004.

| Series I. | | |
|-------------|--------------|------------|
| Weight UBr. | Weight AgBr. | At. wt. U. |
| 3.40006 | 4.57930 | 238.08 |
| 3.91408 | 5.27180 | 238.06 |
| 4.52766 | 6.09791 | 238.09 |
| 5.13497 | 6.91566 | 238.10 |
| 3.73118 | 5.02536 | 238.07 |
| 4.68978 | 6.31652 | 238.06 |
| 3.28480 | 4.42400 | 238.09 |
| 3.91067 | 5.26715 | 238.06 |

Mean, 238.08

| Weight UBr. | Weight Ag. | At. wt. U. |
|-------------|------------|------------|
| 4.52766 | 3.50286 | 238.10 |
| 5.13497 | 3.97256 | 238.12 |
| 4.68978 | 3.62849 | 238.07 |
| 3.28480 | 2.54131 | 238.10 |
| 3.91067 | 3.02567 | 238.07 |
| 4.16254 | 3.22038 | 238.10 |

Mean, 238.09

| Series II. | | |
|-------------|--------------|------------|
| Weight UBr. | Weight AgBr. | At. wt. U. |
| 2.89549 | 3.89900 | 238.18 |
| 2.82823 | 3.80830 | 238.20 |
| 3.95050 | 5.31979 | 238.17 |
| 3.57277 | 4.81110 | 238.17 |
| 3.91948 | 5.27803 | 238.17 |
| 3.77074 | 5.07761 | 238.18 |
| 4.31113 | 5.80562 | 238.15 |
| 3.33325 | 4.48823 | 238.21 |
| 5.14622 | 6.93002 | 238.16 |
| 5.05193 | 6.80279 | 238.18 |
| 5.33502 | 7.18387 | 238.19 |
| 4.84910 | 6.52962 | 238.19 |
| 5.24735 | 7.06581 | 238.19 |
| 4.56095 | 6.14204 | 238.15 |

Mean, 238.18

| Weight UBr. | Weight Ag. | At. wt. U. |
|-------------|------------|------------|
| 3.91948 | 3.03190 | 238.18 |
| 3.77074 | 2.91689 | 238.17 |
| 4.31113 | 3.33505 | 238.15 |
| 5.14622 | 3.98089 | 238.17 |
| 5.05193 | 3.90789 | 238.18 |
| 5.33502 | 4.12698 | 238.17 |
| 4.84910 | 3.75106 | 238.17 |
| 5.24735 | 4.05913 | 238.17 |
| 4.56095 | 3.52825 | 238.16 |

Mean, 238.17

and cooled in nitrogen. The results of Series II are preferred since the salt used in Series I probably contained free bromine. Analysis was effected by comparison with weighed amounts of silver and by weighing the silver bromide formed. Weights are corrected to vacuum.

Neoytterbrium.—Blumenfeld and Urbain¹ have purified the nitrate of this element by fractionation, and give its atomic weight as 173.54. This is higher than that of Auer von Welsbach's "aldebaranium," 173.00.

The atomic weights of thorium, cerium, and beryllium have been discussed from the standpoint of transparency to X-rays by Benoist and Copaux,² that of nebulium by Bourget, Fabry and Buisson³ and Nicholson,⁴ the relations between the atomic weights by Loring.⁵

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY.]

THE DISSOCIATION OF HYDROGEN INTO ATOMS.

[PART II.]

CALCULATION OF THE DEGREE OF DISSOCIATION AND THE HEAT OF FORMATION.

BY IRVING LANGMUIR.

Received December 21, 1914.

The first part of this paper⁶ dealt with experiments on the heat losses from fine tungsten wires in hydrogen at pressures ranging from 0.00 mm. up to atmospheric pressure. The results were given in a series of tables, and form the basis for the present calculation of the degree of dissociation and the heat of formation of molecular hydrogen.

The previous calculations of the dissociation of hydrogen⁷ were based on the use of the equation

$$(3)^8 \quad W_D = SDq_1c_1$$

as described in Part I. The equation itself rests on a firm foundation, but the assumptions previously made in applying it to experimental results are open to serious criticism.

In the first place, it was assumed that the diffusion coefficient D could be calculated with sufficient accuracy from some equations of the kinetic

¹ *Compt. rend.*, 159, 325 (1914).

² *Ibid.*, 158, 689, 859 (1914).

³ *Compt. rend.*, 158, 1017 (1914).

⁴ *Ibid.*, 158, 1322 (1914).

⁵ *Chemical News*, 108, 188, 247, 305; 109, 169; 110, 25 (1914).

⁶ Langmuir and Mackay, *THIS JOURNAL*, 36, 1708 (1914).

⁷ *Ibid.*, 34, 860 (1912). This paper will hereafter be referred to as the "paper of 1912."

⁸ For the derivation of this and some of the following equations, see Part I, or the "paper of 1912." The numbers of the equations are the same as those used in Part I.

theory by the rather arbitrary choice of a value for the mean free path of hydrogen atoms through ordinary molecular hydrogen.

Secondly, it was assumed that the shape factor S in the above equation had the same value as that obtained from the data on the convection losses in hydrogen at temperatures below that at which dissociation occurred.

Thirdly, it was assumed that the hydrogen in the immediate vicinity of the tungsten wire was in chemical equilibrium at a temperature corresponding to that of the wire. In other words, c_1 was taken to be the equilibrium concentration at the temperature of the wire.

And finally, the value of q_1 was found by a method which itself involved any error occurring in D .

Each of the four factors in Equation 3 was therefore liable to error. This was realized and pointed out at the time the calculations were made, but there was then no reason to suspect that any of these sources of error was serious enough to greatly affect the results.

In the present paper we shall endeavor to avoid these arbitrary assumptions and, by a careful analysis of the mechanism of the phenomena occurring in and around the wire, we will attempt to estimate and eliminate the errors which would otherwise occur.

1. Effect of Convection Currents.

In the experiments with hydrogen at atmospheric pressure the effect of convection currents in heating the upper part of the bulb was very noticeable. But in the bulbs with 200 mm. pressure of hydrogen or less, the upper part of the bulb was not as strongly heated as the lower part. It is, in fact, well known that convection currents decrease rapidly in intensity as the pressure is lowered, also that in hydrogen they are very much less pronounced than in other gases. If one considers the cause of convection currents it is evident that the behavior of hydrogen is just what one should expect.

The force producing convection currents is proportional to the difference in the densities of the ascending and descending currents of the gas. Since the density of a gas is equal to pM/RT it is readily seen that the force producing convection is thus proportional to

$$\frac{pM}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{pM}{RT_1} \left(\frac{T_2 - T_1}{T_2} \right).$$

This force is directly proportional to the density of the gas and to the fraction $(T_2 - T_1)/T_2$. As T_2 becomes large this fraction approaches unity as a limit, so that, at very high temperatures, there is little tendency for convection to increase, and even this is largely counteracted by the increasing viscosity of the gas at high temperatures,

The experimental results themselves, however, furnish us with data by which we can estimate the effect of convection currents.

At temperatures below that at which perceptible dissociation of hydrogen occurs, we have seen that the heat losses from the filament are given fairly accurately by the equation (see Table III, Part I).

$$(2) \quad W_C = S(\varphi_2 - \varphi_1).$$

The shape factor S for concentric cylinders is equal to (*Phys. Rev.*, 34, 407 (1912))

$$(7) \quad S = \frac{2\pi}{\ln b/d}$$

where b is the diameter of the film of gas around the wire through which conduction takes place and d is the diameter of the wire.

Let us now substitute the experimentally determined values of S from Table III in this equation, together with the known value of d ($= 0.00706$ cm.) and solve the equation for b . We thus find

| p . | S . | b . |
|---------|-------|----------|
| 750 mm. | 1.25 | 1.08 cm. |
| 200 | 0.88 | 9.0 |
| 100 | 0.72 | 45.0 |
| 50 | 0.56 | 530.0 |

At atmospheric pressure the effective diameter of the film of conducting gas around the tungsten wire is about one centimeter, but at 200 mm. pressure the diameter is already 9 cm., which is larger than the diameter of the bulb (7 cm.). This means that the heat loss from the filament is actually less than if there were no convection currents and the ordinary laws of heat conduction could be applied. At lower pressures the heat loss becomes still less, although we know that the true heat conductivity of gases is independent of the pressure.

These considerations lead us to conclude that the effects of convection currents can be neglected even at pressures as high as 200 mm. We shall see that the decrease in the values of S at the lower pressures is due to a temperature discontinuity at the surface of the wire.

2. The Temperature-drop at the Surface of the Wire.

Kundt and Warburg,¹ in a study of the viscosity of gases at low pressures, showed, both experimentally and theoretically, that there is a certain apparent slipping of the gas along the surface. In gases at atmospheric pressure this effect is very small, but it varies inversely proportional to the pressure and thus becomes very important at low pressures. The thickness of the layer in which this slipping occurs is approximately equal to the mean free path of the gas molecules. Kundt and Warburg predicted, from the analogy between viscosity and heat conduction, that a corresponding discontinuity in temperature at the surface of a solid body

¹ *Pogg. Ann.*, 156, 177 (1875).

would be observed in the case of heat conduction through gases at low pressure.

Over twenty years later Smoluchowski¹ actually observed and studied this temperature drop and developed the theory of it. The temperature drop occurred within a layer about equal in thickness to the free path of the molecules. Smoluchowski found that in some gases, particularly hydrogen, the amount of heat given up to the gas by a solid body was only a fraction of that which should be delivered if each molecule striking the surface reached thermal equilibrium with the solid before leaving it.

Smoluchowski developed the theory of this effect along the lines of two alternative hypotheses, which he denotes by A and B.

Hypothesis A is equivalent to that made more recently by Knudsen.² It assumes, when molecules of a temperature T_1 strike a surface at a higher temperature T_2 , that the molecules leaving the surface have a temperature T which is intermediate between T_2 and T_1 and that the relation holds

$$(8) \quad T - T_1 = \alpha(T_2 - T_1)$$

where α is a number less than unity and is called by Knudsen the "accommodation coefficient."

Hypothesis B is similar to that originally used by Maxwell³ in dealing with the slip of gases. It assumes that, of all the molecules striking the surface, a fraction, f , reaches thermal equilibrium with it, while the fraction $1 - f$ is reflected without change of temperature (or rather velocity).

The two methods give analogous, but quantitatively slightly different results. Smoluchowski⁴ considers that the accuracy of experimental results has not yet been sufficient to distinguish between them, notwithstanding Knudsen's opinion to the contrary, and that in all probability the truth is intermediate between the two.

The formulas developed by Smoluchowski are only adapted to be applied to small differences of temperature and to heat conduction between surfaces whose radius of curvature is large compared to the mean free path of the molecules. In the present experiments, however, we are dealing with very small wires and with temperature drops of sometimes a thousand degrees or more, and we shall therefore need to derive the equations independently. We shall choose a simpler, although less rigorous method, based upon the same principles as those used by Smoluchowski. In this way we shall gain a clearer insight into the phenomena occurring around the wire and will be in a better position to apply similar principles to the problem of calculating the degree of dissociation of the gas.

¹ *Wied. Ann.*, 64, 101 (1898); *Wien. Sitzungsber.*, 108, 5 (1899); *Phil. Mag.*, 46, 192 (1898).

² *Ann. Phys.*, 34, 593 (1911).

³ *Phil. Trans.*, 170, 231 (1879).

⁴ *Ann. Phys.*, 35, 983 (1911).

Theory of Heat Conduction from Small Wires.—Let us consider a small heated wire A (Fig. 1) placed in the axis of a large cylindrical bulb B of diameter b , containing gas at such low pressure that the effects of convection can be neglected. Let T_s be the temperature of the wire and T_1 that of the bulb. If λ represents the length of the mean free path, then the distance which a molecule leaving the wire travels before colliding with other molecules is approximately λ .¹ On the other hand, the molecules striking the wire come from an average distance λ . Let us draw a circle, C (in Fig. 1), of diameter $d + 2\lambda$, around the wire, whose diameter is d and a similar circle D of diameter $b - 2\lambda$.

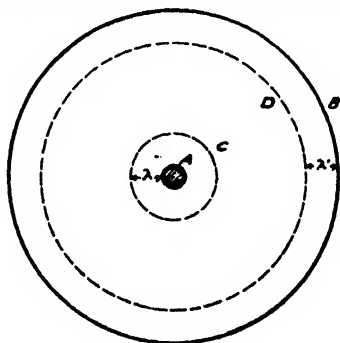


FIG. 1.

We may now look upon the heat conduction from the wire A to the cylinder B as taking place in the following steps:

1. Molecules of gas leave the wire and travel to C, where they are absorbed, and some molecules from C travel to the wire, a certain fraction of these absorbing heat from the wire.
2. From C to D the heat is carried according to the ordinary laws of heat conduction.
3. From D to B the energy is transferred by a simple interchange of molecules in a similar way to the transfer from A to C.

Thus we consider a temperature discontinuity from A to C and from D to B, but a continuous variation of temperature from C to D.

Since we are dealing with small wires in relatively large cylinders, we can readily see that the temperature drop from D to B will always be negligible compared to that from A to D. We shall therefore leave it out of consideration.

Let us represent by T_c the temperature of the gas at C. We can now calculate the temperature drop $T_s - T_c$.²

If we let m be the rate at which the gas comes into contact with the

¹ Knudsen, *Ann. Phys.*, 34, 654 (1911), shows that the temperature of the molecules striking a plane surface corresponds to the temperature of the gas at a distance equal to 0.95 times the mean free path of the molecules. Using more recent data than that available to Knudsen, I calculate from his formulas that this coefficient should be about 1.2. Undoubtedly the coefficient would be somewhat different for very small wires from what it is for plane surfaces, but in any case its order of magnitude is close to unity. Fairly large errors in the value of this coefficient make only very slight differences in the results that are to be obtained by its aid.

² This is somewhat greater than the temperature drop defined by Smoluchowski, for it includes the *normal* temperature difference between A and C.

wire (in grams per sq. cm. per second), then the heat carried from the wire per second will be (per cm. of length)¹

$$(9) \quad W_C = 4.19 \pi d (C_v/M) \alpha (T_2 - T_a)m.$$

where W_C is the heat carried from the wire per unit volume and the coefficient α is the accommodation coefficient, and d is the diameter of the wire.

In order to calculate $T_2 - T_a$ from Equation 9 we must now substitute in it the value of m as given by Equation 5 of Part I, namely,

$$(5) \quad m = \sqrt{\frac{M}{2\pi RT_a}} p.$$

Here M is the molecular weight of the gas, T_a is the temperature of the gas at a distance λ from the wire (at C in Fig. 1).

In the derivation of this formula Maxwell's distribution law was assumed to hold. Where the temperature discontinuity at the surface is as large as in the present experiments the distribution of velocities among the molecules is undoubtedly very complex. The error involved in using this equation must, however, be relatively small.²

Before substituting (5) in (9) let us insert the numerical values of the constants. In (5) we place $M = 2$, $R = 8.32 \times 10^7$ ergs/° C. and express p in mm. of mercury and m in grams per sq. cm. per second. We thus obtain

$$(10) \quad m = \frac{0.0825 p}{\sqrt{T_a}}.$$

In (9) we place $C_v = 5.26$ g. cal. per degree (from 300° to 1500° K.)³ and $d = 0.00706$ cm. This gives, when we combine with (10)

$$(11) \quad T_2 - T_a = 49.6 \frac{W_C \sqrt{T_a}}{\alpha p}.$$

¹ Knudsen shows that this should be multiplied by $4/3$, since the average velocity of all the molecules striking any surface is greater than the average velocity of the molecules in the body of the gas. This is due to the fact that the molecules of high velocity have a much greater chance of striking a surface than those of low velocity. On the other hand, for polyatomic gases the exchange of rotational energy is not complete and, therefore, a quantity less than should be substituted in the above equation. According to Smoluchowski, the combined effect of these two corrections would lead to a coefficient of $16/15$ in place of the $4/3$ mentioned above. For the present purpose this small correction may be neglected.

² With large differences of temperature over distances comparable with the free path, another effect, which we may call the radiometer effect, enters to render Equation 5 inaccurate. The rapidly moving molecules leaving the wire tend to drive back the slower incoming molecules and thus to decrease the rate at which the molecules strike the wire. Although this effect would be very important if we were dealing with large flat surfaces, calculation shows that in our present experiments, where only fine wires are employed, this error is always less than 5% and usually much less than this. It has, therefore, been neglected.

³ The letter K is used to denote temperatures on the absolute scale (Kelvin).

This equation enables us to estimate the difference between the temperature of the wire and that of the gas molecules which strike its surface.

We may also calculate the temperature of the gas molecules striking the wire in another way. Between the surface C (Fig. 1) and the bulb, the ordinary laws of heat conduction must apply at pressures below that at which convection occurs. Thus we may place, according to (2) and (7)

$$(12) \quad W_C = \frac{2\pi}{\ln b/(d + 2\lambda)} (\varphi_a - \varphi_1).$$

If we know the effective diameter of the bulb and the mean free path of the gas molecules, we can calculate from this equation the value of $(\varphi_a - \varphi_1)$, and since φ is a known function of the temperature, this in turn will enable us to determine T_a .

Let us now calculate T_a from our experiments with hydrogen by means of Equations 11 and 12. For this purpose we will choose the data obtained at 1500° K., for at this temperature there is no appreciable dissociation and the temperature measurements are more accurate than at lower temperatures. These data, as taken from Tables I and II of Part I, are given below in Table V in the second column. The figures represent the watts per centimeter carried by the hydrogen from a wire at 1500° K. The first column gives the pressure of hydrogen in mm. of mercury. In the third column are the values of T_a calculated by Equation 11.

TABLE V.--WIRE IN HYDROGEN.

| $T_2 = 1500.$ | | | $\alpha = 0.19.$ | | | |
|---------------|--------------|----------------------|------------------------|--------------------------------|------------|----------------------|
| 1. $p.$ | 2. $W_C.$ | 3. T_a by (11). | 4. λ cm. | 5. $\varphi_a - \varphi_1.$ | 6. $b.$ | 7. T_a by (12). |
| 750 | 5.50 | 1428 | 0.0001 | [4.10] | 0.78 | (1428) |
| 200 | 3.90 | 1316 | 0.0003 | [3.53] | 1.87 | (1316) |
| 100 | 3.13 | 1216 | 0.0006 | [3.03] | 3.7 | (1216) |
| 50 | (2.52) | 1071 | 0.0011 | 2.39 | [3.7] | 1070 |
| 25 | 1.92 | 900 | 0.0020 | 1.78 | [3.7] | 920 |
| 10 | (0.94) | 806 | 0.0037 | 0.83 | [3.7] | 660 |
| 4.4 | 0.47 | 742 | 0.0063 | 0.46 | [9.0] | 520 |
| 1.1 | 0.19 | 495 | 0.020 | 0.16 | [9.0] | 390 |
| 0.207 | 0.050 | 341 | 0.094 | 0.03 | [9.0] | 317 |
| 0.039 | 0.009 | 360 | 0.5 | 0.003 | [9.0] | 302 |
| 0.015 | 0.004 | [300] | 1.3 | 0.001 | [9.0] | 300 |

The accommodation coefficient α was calculated from the data at the lowest pressure (0.015 mm.) by substituting $T_a = 300$;¹ $T_2 = 1500$; $W_C = 0.004$; and $p = 0.015$ in Equation 11. This gave $\alpha = 0.19$, which, when substituted in (11) gave

$$(13) \quad T_2 - T_a = 260 (W_C/p) \sqrt{T_a}.$$

¹ That it is justifiable to place $T_a = 300$ at these lowest pressures is shown by the results obtained below and given in the seventh column.

The values of T_a given in the third column of Table V were obtained by solving these quadratic equations.

The free path of hydrogen molecules at 0° C. and 1 mm. pressure is 0.0135 cm., according to O. E. Meyer. The free path varies with the temperature according to Sutherland's formula, but for the present purpose it is accurate enough to assume that it is inversely proportional to the density. The fact that at low pressures the molecules leaving the surface at a much lower temperature than the surface temperature is a serious complication of the free path leading to the formula

$$(14) \quad \lambda = \frac{40.5 \times 10^{-6}}{p} \sqrt{\frac{2T_2}{T_2 + T_a}}$$

This equation was used to calculate the free paths given in Col. 4 of Table V.

At the higher pressures the effects of convection currents cannot be neglected, so that Equation 12 would not be expected to hold accurately under these conditions. However, even in the case of convection from small wires in the open air we may profitably look upon the phenomena as consisting essentially in conduction through a film of stationary gas of a certain thickness. If we adopt this view-point, Equation 12 applies *even at the higher pressures, but b then no longer represents the diameter of the bulb, but becomes the effective diameter of the film of gas through which conduction occurs.* To determine the value of b we need only substitute the values of W_C , d , λ and $\varphi_a - \varphi_1$ in Equation 12 and solve for b . For this purpose the values of $\varphi_a - \varphi_1$ were calculated from T_a , for the pressures of 760 to 100 mm., and are given in Table V (Col. 5) in brackets. These then served to calculate b from (12). At the lower pressures (50-10 mm.) it was then assumed that convection currents were absent and that b was therefore independent of the pressure and equal to the value 3.7 cm., as found at 100 mm. Below 10 mm. b was placed equal to the diameter of the bulb, for in these experiments a straight wire in a cylindrical bulb was used.

The values of $\varphi_a - \varphi_1$ at the lower pressures were obtained from (12) by substituting in it W_C , b , d and λ as given in the table. The results are given in Col. 5 (without brackets) and were used to calculate the corresponding values of T_a given in the seventh column.

By comparison of Cols. 3 and 7, it is seen that there is reasonably good agreement between the values of T_a calculated by these entirely independent methods. The fact that the temperature drop at the surface of the wire ($T_2 - T_a$) is so large, even at the higher pressures, is the reason

¹ Derived from the equations given on page 260 of Meyer's "Kinetische Theorie der Gase," German edition of 1899.

for the variation of the shape factor (given in Table III at the heads of the columns).

The accommodation coefficients α is found above to be equal to 0.19. This is considerably lower than the value 0.36 found by Knudsen for hydrogen in contact with polished platinum at approximately room temperature.

The results given in Col. 6 of Table V show that the effective thickness of the layer of "stationary" gas around the wire increases as the pressure decreases from 750 to 100 mm., owing to convection currents. At lower pressures, however, the results indicate that there is no further change in b . If the lamps used in these experiments had contained a long, straight filament in the axis of a cylindrical bulb, then b should be equal to the diameter of the bulb. Actually, however, the filament was a short loop only about 3 cm. long. The resulting divergence of the lines of heat flow would tend to increase the shape factor, which would be equivalent to a decrease in diameter of a cylindrical bulb. Hence the value of 3.7 cm. found above for b is in as close agreement with the actual bulb diameter (7 cm.) as the experimental conditions would seem to warrant.

Nitrogen.—Similar calculations from the data given in Table I, for a filament at a temperature of 2400° in nitrogen yield the results shown in Table VI. The values of T_a in Col. 3 were obtained from a formula similar to (11) in which, however, the coefficient 49.6 was replaced by 166, corresponding to the different molecular weight and specific heat of nitrogen. The columns of Table VI correspond exactly to those of Table V.

It is seen by the variation of b that the effect of convection is much more marked than with hydrogen and persists at pressures even as low as 50 mm.

TABLE VI.—WIRE IN NITROGEN.

| $T_s = 2400.$ | | | | | $\alpha = 0.60.$ | |
|---------------|-----------|--------------|------------------------|--------------------------------|------------------|----------------------|
| 1. $p.$ | 2. WC. | 3. $T_a.$ | 4. λ cm. | 5. $\varphi_a - \varphi_1.$ | 6. $b.$ | 7. T_a by (12). |
| 750 | 2.46 | 2356 | 0.0001 | [1.68] | 0.54 | (2356) |
| 200 | 2.06 | 2264 | 0.0003 | [1.56] | 0.89 | (2264) |
| 100 | 1.87 | 2160 | 0.0006 | [1.44] | 1.01 | (2160) |
| 50 | 1.34 | 2064 | 0.0011 | [1.32] | 4.4 | (2064) |
| 10 | 0.75 | 1580 | 0.0046 | 0.74 | [8] | 1530 |
| 1 | 0.16 | 1000 | 0.031 | 0.12 | [8] | 650 |

The accommodation coefficient is much larger than that of hydrogen, but is again less than that given by Knudsen (for air) at room temperature.

The agreement between the values of T_a calculated by the two independent methods, in both Tables V and VI, is sufficiently good to show that the general theory of heat conduction and convection used in making the calculations can safely be applied to the case of fine tungsten wires in hydrogen and nitrogen at all pressures. Evidently the heat conductivities

of these gases, within the ranges of temperature considered above, vary with the temperature in the way that is to be expected from their behavior at ordinary temperatures.

3. Concentration Drop at the Surface of the Wire.

We have seen that the temperature of the layer of gas next to the wire may be very much lower than that of the wire itself. To assume that these two temperatures are equal, which amounts to assuming temperature equilibrium at the surface of the wire, would lead to entirely erroneous results.

The diffusion of one gas through another is a phenomenon closely related to heat conduction. In the case of the evaporation of a solid surrounded by a gas, where the vapor must diffuse outward through the gas, the partial pressure of the vapor at the surface of the solid will be less than that of the saturated vapor. In other words, there will be a "concentration-drop" at the surface, just as there is a "temperature drop" in the analogous case of heat conduction, and a "slip" in gases where viscosity effects are involved. Analogy suggests that this concentration drop will be inversely proportional to the pressure.

In the previous calculations of the dissociation of hydrogen it was assumed that the concentration of the hydrogen atoms close to the wire, was that corresponding to equilibrium at the temperature of the wire. As the experiments underlying these calculations were made at atmospheric pressure, this assumption involved no serious error, but at the low pressures which we are now to consider, such an assumption would render the results worthless.

In analyzing the effect of the surface concentration drop in our present experiments, we may follow methods entirely analogous to those which we adopted in estimating the temperature drop.

Let us consider the mechanism of the phenomena occurring on and around a tungsten wire surrounded by hydrogen, and heated to such a high temperature that the hydrogen is partly dissociated. The hydrogen molecules striking the surface come from an average distance of approximately λ (the mean free path). A certain proportion of these molecules leave the surface without change (reflected) and another portion is absorbed by the wire and may thus be dissociated. Similarly, hydrogen atoms striking the filament may be absorbed or reflected. The hydrogen which is absorbed probably reaches chemical equilibrium within the wire and the atoms and molecules in certain proportions diffuse out and away from the wire. We assume that the hydrogen not absorbed undergoes no chemical change.

Let m_2 represent the rate at which hydrogen molecules strike the surface of the filament (in grams per sq. cm. per second) and m_1 be the corresponding rate for the hydrogen atoms. Let $\alpha_1 m_1$ be the rate at which the hydrogen atoms are absorbed by the wire and $\alpha_2 m_2$ be the rate at which the

molecules are absorbed. Now in a stationary condition the total amount of hydrogen escaping from within the wire must be equal to the rate at which it is absorbed. We may look upon the surface of the wire as the boundary of a space containing hydrogen in equilibrium. The rate at which the hydrogen atoms in the metal reach the surface (from within) we shall call n_1 , and the corresponding rate for the molecules n_2 . Similarly, we shall let $\beta_1 n_1$ be the rate at which atoms escape from the metal and $\beta_2 n_2$ the rate at which molecules escape. Then in a stationary state we have

$$(15) \quad \beta_1 n_1 + \beta_2 n_2 = \alpha_1 m_1 + \alpha_2 m_2.$$

We assume that the coefficients α and β are constant; that is, that they are independent of m and n , although they may vary with the temperature.

The energy (watts) carried away from the wire (per cm.) because of the dissociation, we have called W_D . If q_1 be the heat (calories) necessary to dissociate 1 g. of hydrogen, then we have

$$(16) \quad W_D = 4.19 \pi d q_1 (\alpha_2 m_2 - \beta_2 n_2).$$

Here d is the diameter of the wire. The quantity in parenthesis is the difference between the rates at which hydrogen molecules are absorbed and are given up by the wire and therefore is equal to the rate at which hydrogen is dissociated.

If we place

$$(17) \quad \omega = W / (4.19 \pi d q_1)$$

then (16) becomes

$$(18) \quad \omega = \alpha_2 m_2 - \beta_2 n_2$$

Combining this with (15), we obtain

$$(19) \quad \omega = \beta_1 n_1 - \alpha_1 m_1$$

whence

$$(20) \quad \begin{cases} \beta_1 n_1 = \alpha_1 m_1 + \omega \\ \beta_2 n_2 = \alpha_2 m_2 - \omega \end{cases}$$

Now we have assumed that equilibrium exists between the hydrogen atoms and molecules absorbed by the wire. According to the law of mass action, the concentration of the hydrogen molecules in the metal is proportional to the square of the concentration of the atoms. But n_2 and n_1 must be proportional to these concentrations. From Equation 20 we thus obtain

$$(21) \quad (\alpha_1 m_1 + \omega)^2 = A(\alpha_2 m_2 - \omega).$$

Here A is a constant which is proportional to the dissociation constant of hydrogen dissolved in the metal. We may now obtain a relation between this quantity A and the true dissociation constant K of gaseous hydrogen (outside the wire).

We have

$$(22) \quad K = (p_1')^2 / p_2'$$

where p'_1 and p'_2 are, respectively, the partial pressures of hydrogen atoms and molecules corresponding to equilibrium in the gaseous phase.

By Equation 5 (Part I) we have from (22) by placing $M_1 = 1$ and $M_2 = 2$

$$(23) \quad K = \sqrt{4\pi RT_2} (m'_1)^2 / m'_2$$

where T_2 is the temperature of the filament.

On the other hand, if we place $\omega = 0$ in (21), we obtain the condition for equilibrium. In this case (21) becomes

$$(24) \quad A = (\alpha_1^2 / \alpha_2) \cdot (m'_1)^2 / m'_2$$

and by combining this with (23) we find the desired relation between A and K

$$(25) \quad K = \sqrt{4\pi RT_2} (\alpha_2 / \alpha_1^2) A.$$

If we now substitute in (21) the values of m_1 and m_2 from Equation 5 and then combine with (25), we obtain

$$(26) \quad K = \sqrt{T_2 / T_a} \frac{(p_1 + \omega \sqrt{2\pi RT_a} / \alpha_1)^2}{p_2 - \omega \sqrt{2\pi RT_a} / \alpha_2 \sqrt{2}}.$$

Here T_a is the temperature of the gas around the wire at a distance λ from it (corresponding to circle C of Fig. 1). When $\omega = 0$ and $T_a = T_2$ this equation reduces to the ordinary form of the law of mass action. The "drop in concentration" corresponding to the drop in temperature previously considered is equivalent to $\omega \sqrt{2\pi RT_a} / \alpha_1$.¹

In the above equation p_1 and p_2 are the partial pressures of hydrogen atoms and molecules at a distance λ from the wire.

Let us substitute the numerical values of the constants involved in (26). If we express p in mm. of mercury, then the factor $\sqrt{2\pi R}$ is 17.15. If we place $d = 0.00706$ cm. (the diameter of the wire) in (17) we find $\omega = 10.8 W_D / q_1$. Substituting these in (26), we obtain

$$(27) \quad K = \sqrt{T_2 / T_a} \frac{(p_1 + 185 W_D \sqrt{T_a} / \alpha_1 q_1)^2}{p_2 - 131 W_D \sqrt{T_a} / \alpha_2 q_1}.$$

Here p is expressed in mm., W_D in watts per cm., and q_1 in calories per gram.

4. Diffusion of Atomic Hydrogen away from the Wire.

In the calculation of the temperature drop around a wire in hydrogen, we used two methods which led to Equations 11 and 12, respectively. Similarly, in the calculation of the concentration drop, two methods may be used. The method adopted above in obtaining Equation 27 is analogous to that used in deriving (11), whereas the following method corresponds to that employed in obtaining (12).

In the "paper of 1912" it was shown that

$$(3) \quad W_D = SDq_1c_1$$

¹ Expressed as partial pressure instead of concentration.

Here c_1 is to be expressed in mols per cc., and is equal to

$$(28) \quad c_1 = p_1/RT.$$

The diffusion coefficient varies with the temperature according to Sutherland's formula, but at the high temperatures we are dealing with, this becomes equivalent to stating that the diffusion coefficient varies with the $3/2$ power of the temperature. We will assume that the diffusion coefficient of hydrogen atoms through molecular hydrogen varies in this way with the temperature, although we shall avoid assumptions as to its actual magnitude. Since the diffusion coefficient is inversely proportional to the pressure, we may thus place:

$$(29) \quad D = D_0 (T_a/273)^{3/2} \cdot (760/P)$$

where D_0 is the diffusion coefficient at 0° and 760 mm. pressure, and T_a is the temperature of the gas around the wire (*i. e.*, at the distance λ from it).

Combining (29), (28), and (3) we obtain, after substituting the numerical value for R

$$(30) \quad W_D = 11.3 \times 10^{-6} S q_1 D_0 \sqrt{T_a} p_1/P.$$

This equation gives us the desired relation between p_1 , the partial pressure of hydrogen atoms around the wire, and W_D . It enables us to calculate the degree of dissociation if we know S , q_1 and D_0 .

5. Equations Involved in Calculating the Dissociation Constant, etc.

Equation 27 has given us a means of calculating the dissociation constant from the partial pressures of hydrogen atoms and molecules around the wire. These partial pressures may be expressed in terms of the diffusion constant by means of Equation 30. By combining these two equations it is possible to obtain a general solution of the problem in the following form:

$$(31) \quad K = \sqrt{T_2/T_a} \frac{W_D^2 (BP + E)^2}{P - W_D (BP + C)}$$

where

$$(32) \quad B = 88500/(SD_0 q_1 \sqrt{T_a}) \text{ cm. per watt}$$

$$(33) \quad C = 131 \sqrt{T_a}/(\alpha_2 q_1) \text{ mm. of Hg per watt/cm.}$$

$$(34) \quad E = 185 \sqrt{T_a}/(\alpha_1 q_1) \text{ mm. of Hg per watt/cm.}$$

The dissociation constant K increases rapidly with the temperature, while B , C and E depend only to a small degree on the temperature, and therefore we see by (31) that at low temperatures W_D will increase approximately proportional to \sqrt{K} . At high temperatures, however, the two terms in the denominator must tend to become equal, so that W_D would approach a limiting value. From Equation 31 we can readily derive simple equations for these limiting cases.

At low temperatures the second term of the denominator is negligible, so that

$$(35) \quad K = \sqrt{T_2/T_a} \ W_D^2 (BP + E)^2/P.$$

At low pressures this gives:

$$(36) \quad W_D = \sqrt[4]{\frac{T_a}{T_2}} \sqrt{\frac{PK}{E}}.$$

At high pressures (here $T_a = T_2$).

$$(37) \quad W_D = \sqrt{K/P/B}.$$

At intermediate pressures W_D increases to a maximum. Differentiating (35) with respect to P and placing $dW_D/dP = 0$ leads to following maximum value of W_D (here $T_a = T_2$):

$$(38) \quad W_{\max.} = \sqrt{K/4BE}.$$

The pressure at which this maximum occurs is

$$(39) \quad P' = E/B.$$

At high temperatures W_D increases so that ultimately $W_D(BP + C)$ becomes nearly equal to P . Beyond this value it cannot go. Therefore, at high temperatures W_D must gradually approach a limiting value. This limit is

$$(40) \quad \begin{array}{l} \text{at low pressures} \\ W_D = P/C \end{array}$$

$$(41) \quad \begin{array}{l} \text{at high pressures} \\ W_D = 1/B. \end{array}$$

The higher the pressure the higher is the temperature at which W_D approaches its limiting value.

We shall see that the case where $C = E$, is of special importance. If we make this substitution in (31) and place

$$(42) \quad F = BP + E$$

we obtain the very simple equation

$$(43) \quad K = \sqrt{T_2/T_a} \frac{F^2 W_D^2}{P - F W_D}.$$

At higher pressures T_a becomes practically equal to T_2 , so the equation is still further simplified.

$$(43a) \quad K = F^2 W_D^2 / (P - F W_D).$$

Comparing this with (22), we see that FW_D is equal to the partial pressure of hydrogen atoms corresponding to equilibrium at the temperature of the filament. The degree of dissociation of the hydrogen in equilibrium is therefore FW_D/P .

At low temperatures we have already found expressions for the maximum value of W_D and the pressure at which this occurs. On the assumption that $C = E$ we may now find more general expressions applicable even

at high temperatures. Differentiating (42) and (43a) with respect to P , placing $dW_D/dP = 0$ and solving the resulting equation together with (31), we obtain

$$(44) \quad W_{\max.} = 1/(B + \sqrt{4BE/K}).$$

$$(45) \quad P' = (E/B) + \sqrt{EK/B}.$$

6. Calculation of Results from Experimental Data.

The equations that have been derived in the preceding section give us means of calculating the coefficients B , C and E , and in this way of determining the dissociation constant K . Thus from the experiments at low pressures and at low temperatures it should be possible by (36) to find the ratio $\sqrt{K} : E$. Experiments at high pressures give by (37) $\sqrt{K} : B$, while those at high temperatures and low pressures give C according to (40). At high pressures and high temperatures we should then obtain B by (41). By combining these results it would thus be possible to find the actual values of B , C , E and K , separately. In practice, however, this method gives difficulty, because the experiments do not cover a sufficiently wide range of pressures or temperatures to allow these limiting equations to hold accurately. Furthermore, the values of W_D obtained under the extremes of temperature or pressure are often subject to unusually large experimental error, and it is unwise to use such data exclusively for the determination of the coefficients. A third difficulty is that Equations 36, 37, 40 and 41 all involve to some extent T_a , the temperature of the gas around the wire, which is not accurately known.

The method finally adopted to determine the coefficients B , C and F has been chosen because of its relative freedom from these difficulties.

1. **The Value of C .**—According to our theory, at very low pressures, W_D does not increase indefinitely with rising temperature, but approaches a limiting value equal to P/C (Equation 40). If we examine the experimental data of Table III we see, in fact, that W_D at the three lower pressures, 0.015, 0.039 and 207 mm., becomes constant at temperatures over 2700°. This is also readily seen from Fig. 2, in which $\log W_D$ has been plotted against $1/T$. The limiting value of W_D at high temperatures for each of these pressures is given in the following table, along with the ratio P/W_D , which, according to (40), is equal to C :

TABLE VII.

| P . | W_D . | $C = P/W_D$. | T_a . |
|---------|---------|---------------|---------|
| 0.015 | 0.18 | 0.0835 | 300 |
| 0.039 | 0.47 | 0.083 | 300 |
| * 0.207 | 1.85 | 0.112 | 545 |

The constancy of C at the lower pressures and its increase at the higher pressure, is in full accord with Equation 33, which states that C is proportional to $\sqrt{T_a}$. At very low pressures T_a must be equal to the tempera-

ture of the bulb (300° K.), just as it was at lower filament temperatures (see Table V). At higher pressures, however, where the hydrogen atoms recombine long before reaching the surface of the bulb, the heat evolved raises the temperature of the gas considerably. At the lower pressures, however, we may safely place $T_a = 300$, and we then find, by comparing Table VII with Equation 33:

$$(46) \quad C = 0.0048 \sqrt{T_a}$$

$$(47) \quad \alpha_2 q_1 = 27300$$

This indicates, since by definition α_2 cannot exceed unity, that q_1 must be greater than 27300, or the heat of formation of 2 g. of hydrogen molecules, must be greater than 54600 calories.

If we compare (46) with the value $C = 0.112$ obtained for $P = 0.207$, we find $T_a = 545$. This is, as we shall see later, an entirely reasonable value.

2. Calculation of an Approximate Value of q_1 .—If we can determine q_1 , then by (47) we can calculate α_2 . This will, in a certain measure, give us a check on our theory, for we know that α_2 cannot exceed unity.

To calculate q_1 , we may make use of van't Hoff's equation

$$(48) \quad d \ln K / dT = q / RT^2.$$

Here q is the heat of reaction at constant pressure since K is expressed in terms of partial pressures. The relation between q and q_1 is

$$(49) \quad q = 2q_1 + RT.$$

If we use ordinary logarithms in place of naperian and substitute $R = 1.98$ calories, we may write Equation 48 as follows:

$$(50) \quad d \log K / d(1/T) = -q / 4.57$$

Since q varies so little with the temperature, we should, according to (50), obtain practically a straight line if we plot $\log K$ against $1/T$. The slope of the line would then be $q/4.57$, from which, by (49), we could calculate q_1 . The slope of this line, however, would be the same if we plot the logarithm of any quantity proportional to K , instead of the logarithm of K itself. If we could assume that $T_a = T_2$ and that B and E were independent of the temperature, then we see from (35) that W_D should be proportional to K . The values of q_1 that we might thus obtain by plotting $\log W_D$ would not be very accurate, because the above assumptions are not strictly correct. However, by using Equation 38, which gives us a relation between K and W_{\max} , we avoid these difficulties. By (32) and (34) we see that the factor BE is independent of T_a and T_2 , so that K is strictly proportional to W_{\max} . Another important advantage in using this equation in determining q is that it does not involve a knowledge of the pressure within the bulb. It should be remembered that in the experiments at pressures of 10 mm., and above, the pressures

of the hydrogen as given in Table III were not measured while the filaments were heated, but were the pressures at which the bulbs were sealed at room temperature. The actual pressures in the bulbs during the experiment must have been considerably higher.¹

It is clear, however, that this uncertainty in the pressure does not affect $W_{\max.}$ nor the accuracy of K calculated from it by (38).

By examining Table III we see, as the pressure increases, that W_D increases to a maximum and then decreases. In the following table are the maximum values of W_D corresponding to various temperatures as given in Table III:

TABLE VIII.

| T. | $W_{\max.} = \sqrt{K/4BE.}$ | T. | $W_{\max.} = \sqrt{K/4BE.}$ |
|------|-----------------------------|------|-----------------------------|
| 2000 | 1.3 | 2500 | 12.5 |
| 2100 | 2.4 | 2600 | 16.7 |
| 2200 | 4.0 | 2700 | 22.7 |
| 2300 | 6.1 | 2800 | 30.0 |
| 2400 | 8.9 | | |

By plotting $2 \log W_{\max.}$ against $1/T$ we obtain in fact an almost perfectly straight line. From the slope of this line we calculate by (50) that $q = 85500$ calories. If we take $T_2 = 2400$ (the center of the range of temperatures in the experiments), we then find by (49)

$$(51) \quad q_1 = 40300 \text{ calories.}$$

3. Calculation of α_2 and Lower Limit for E .—Substituting (51) in (47), we obtain

$$(52) \quad \alpha_2 = 0.68.$$

This means that 68% of all the hydrogen molecules which strike the filament at high temperatures are absorbed by the filament.

If we substitute (51) in (34), we obtain

$$(53) \quad E = 0.0046 \sqrt{T_2}/\alpha_1.$$

Since α_1 cannot exceed unity, E must be greater than $0.0046 \sqrt{T_2}$.

The coefficient α_1 gives the fraction of the hydrogen atoms striking the filament which dissolve in it or are absorbed by it. There is a strong probability that this fraction should be very close to unity, for there is every reason to think that hydrogen atoms would be absorbed by a metal surface much more readily than the molecules, and we have just seen that 68% of the latter are absorbed. We shall see, however, that there is another way of estimating the value of α_1 .

4. Upper Limit for B .—According to (41), the limit which W_D approaches at high temperatures does not increase indefinitely with the pressure,

¹ In some of the experiments at a pressure of 100 mm. of hydrogen, the bulbs became so hot at the higher filament temperatures that the glass softened and sucked in slightly. In another experiment the bulb was immersed in water to keep it cool. This cooling did not have any perceptible effect on the value of W_D .

but ultimately becomes equal to $1/B$. By examining the results given in Table III for the higher pressures we see that W_D does not become constant even at the highest temperatures. This merely indicates that $1/B$ must be considerably greater than 117, the highest value of W_D observed. Or in other words, B must be less and probably much less than $1/117$, or 0.008.

5. Estimation of Ratio $E:B$.—According to (39) at low filament temperatures the fraction E/B should be equal to the pressure at which the maximum values of W_D occur. By referring to Table III we see that the highest values of W_D are observed at 50 mm. pressure. At the lower temperatures there is evidence that the maximum should lie at a pressure rather lower than 50 mm., although above 25 mm. The lack of experimental data at intermediate pressures makes it impossible to determine this pressure with much accuracy, but, making allowance for the heating of the gases in the bulb, it is probable that the true pressure at which the maximum W_D would occur is approximately 50 mm. From this we may conclude that $E/B = 50$.

6. Most Probable Values of E and α_1 .—Since B must be considerably less than 0.008 and E/B is equal to 50, we may conclude that E must be considerably smaller than 50×0.008 or 0.40. We have already seen that E must be greater than $0.0046 \sqrt{T_a}$. If we take $T_a = 2500$, E would have to be greater than 0.23. Therefore, E must lie between the comparatively narrow limits 0.23 and 0.40. There is, however, no reason for thinking that E must be greater than the lower limit, whereas there is evidence that it is considerably less than the upper limit. The most probable value of E is therefore obtained by placing $\alpha_1 = 1$ in (53). The value thus obtained is, however, almost identical with the value of C given by (46). We have seen from (43) that the mathematical treatment is much simplified if $C = E$. The small difference between 0.0048 and 0.0046 is well within the experimental error, so that for convenience we may place

$$(54) \quad C = E = 0.0048 \sqrt{T_a}.$$

7. Calculation of K from Low Pressure Data.

By the aid of these values of C and E we may calculate K from (43). We have seen that at high temperatures B is less than 0.008. Taking Equation 32 into consideration, we may thus conclude that B must always be less than $0.47/\sqrt{T_a}$. At very low pressures $T_a = 300$, so that under these conditions B might be as large as 0.027. At similarly low pressures $E = 0.083$. At a pressure $P = 0.207$ the term BP in (42) is less than 0.005 and may be neglected as compared to E in calculating F . We may thus calculate K from (43) without knowing the value of B , provided we use the data at pressures of 0.207 mm. and lower.

Table IX gives the results of such calculations from the data at the

lowest pressures. The values of K were calculated from the corresponding values of W_D by Equation 43, placing $F = E$. At 0.015 and 0.039 mm. pressure, T_a was placed equal to 300° , but at 0.207 mm. the values of T_a used in the calculation were those given in the next to the last column of the table.

TABLE IX.—DISSOCIATION CONSTANT OF HYDROGEN FROM LOW PRESSURE DATA.

| T. | P = 0.015 mm. | | P = 0.039 mm. | | P = 0.207 mm. | | |
|------|---------------|----------------------|---------------|----------------------|---------------|---------|----------------------|
| | W_D . | K . | W_D . | K . | W_D . | T_a . | K . |
| 1800 | 0.007 | 58×10^{-8} | 0.019 | 165×10^{-8} | 0.068 | 317 | 501×10^{-8} |
| 1900 | 0.013 | 210×10^{-8} | 0.05 | 1.2×10^{-3} | 0.15 | 329 | 2.1×10^{-3} |
| 2000 | 0.025 | 870×10^{-8} | 0.09 | 4.6×10^{-3} | 0.27 | 347 | 7.5×10^{-3} |
| 2100 | 0.048 | 3.9×10^{-3} | 0.14 | 13×10^{-3} | 0.45 | 372 | 25×10^{-3} |
| 2200 | 0.085 | 17×10^{-3} | 0.20 | 34×10^{-3} | 0.65 | 400 | 64×10^{-3} |
| 2300 | 0.112 | 42×10^{-3} | 0.27 | 85×10^{-3} | 0.90 | 430 | 160×10^{-3} |
| 2400 | 0.139 | 112×10^{-3} | 0.35 | 250×10^{-3} | 1.17 | 460 | 380×10^{-3} |
| 2500 | 0.169 | | 0.40 | 1.07 | 1.48 | 500 | 1.17 |
| 2600 | 0.179 | | 0.45 | 2.5 | 1.71 | 520 | 2.6 |
| 2700 | 0.180 | | 0.47 | | 1.84 | 540 | |
| 2800 | 0.180 | | 0.47 | | 1.85 | 540 | |
| 2900 | 0.180 | | 0.47 | | 1.85 | 540 | |

The choice of $T_a = 300$, at the lowest pressures and the tabulated values at 0.207 mm., was based upon calculations similar to those previously employed in obtaining the temperature drop around a wire at low pressures. Thus we may calculate $\varphi_a - \varphi_1$ according to (12), substituting, however, $W_C + W_D$ in place of W_C . The data for the calculation, together with the results, are given in Table X. The values of $W_C + W_D$ were

TABLE X.

| P. | λ . | S. | $W_C + W_D$ at 2800. | $\varphi_a - \varphi_1$. | $b = 9$ cm. T_a . |
|-------|-------------|-----|----------------------|---------------------------|------------------------|
| 0.015 | 1.3 cm. | 5.0 | 0.19 | 0.038 | 321 |
| 0.039 | 0.5 | 2.8 | 0.50 | 0.18 | 400 |
| 0.207 | 0.1 | 1.7 | 1.98 | 1.19 | 760 |
| 1.1 | 0.018 | 1.2 | | | ... |
| 4.4 | 0.004 | 1.0 | | | ... |

taken directly from Table II. In this calculation it is assumed that the hydrogen atoms leaving the filament all recombine to form molecules within a distance λ from the filament and that the heat thus liberated is carried to the bulb by ordinary heat conduction. This assumption, of course, cannot correspond exactly with the facts, but would lead to too high a value for T_a . It is therefore not surprising that the value $T_a = 760$ found at 0.207 mm. should be higher than the value $T_a = 545$ previously calculated by Equation 46 from the data of Table VII. Taking the value $T_a = 545$ as being correct and making a proportionate change in the corresponding values of $\varphi_a - \varphi_1$, we obtain the values of T_a given in Table IX. At the lower pressures the values of T_a are so close to 300° that it

is not worth while to take into account the departures from this temperature.

Before discussing the values of K of Table IX, we shall first attempt to calculate K from the data at pressures of 1.1 and 4.4 mm.

At these higher pressures there is more uncertainty as to the value that should be assigned to T_a . We may, however, adopt a method similar to that we employed to calculate T_a at a pressure of 0.207 mm. In the latter case at very high temperatures W_D became independent of T showing that the denominator in Equation 31 was practically zero. This led to Equation 40, from which we determined C and then by (33) we solved for T_a . At the pressures above 0.207 mm., however, W_D does not reach a constant value at the highest temperatures, although it shows a distinct tendency to do so. This is readily seen from Fig. 2, where $\log W_D$ has been plotted against $1/T$ for the data at pressures up to 4.4 mm. At the three lower pressures the curve becomes horizontal at the highest temperatures, but at 1.1 mm. the temperatures reached were not high enough to give the maximum value of W_D . From the degree of curvature or the change of slope, we may, however, estimate the value of C and in this way find T_a .

By substituting the value of K from (43) in the modified form of van't Hoff's Equation 50 and carrying out the indicated operations, we obtain (considering F as constant and $T_a = T_2$)

$$(55) \quad \frac{2d \ln W_D}{d(1/T)} + \frac{F dW_D/d(1/T)}{P - FW_D} = \frac{q}{R}.$$

If we let $-U$ be the slope of the curve obtained by plotting $\log W_D$ against $1/T$, then the first term of this equation becomes equal to $-2 \times 2.30 U$ and in the second term we find $dW_D/d(1/T) = -2.30 U W_D$. Substituting these values in the equation and solving for U we find (since $R = 1.98$)

$$(56) \quad U = \frac{q}{4.57} \left(\frac{P - FW_D}{2P - FW_D} \right).$$

At lower temperatures FW_D becomes negligibly small compared to P , so that U approaches a definite limit U_0 which is equal to $0.109 q$. From this relation we can eliminate q from (56) and then solve for F , with the result:

$$(57) \quad F = \frac{P}{W_D} \cdot \frac{U_0 - U}{U_0 - 1/2U}.$$

From the curve of Fig. 2 we find the slope of the curve at 2700° ($1/T = 0.000370$) to be 3760. We have already calculated that q is approximately 85000 and from this we obtain $U_0 = 0.109$, $q = 9300$. Substituting these in (57), together with W_D (at 2700°) = 5.7 and $P = 1.1$, we obtain

$$F = 0.145.$$

According to (42) $F = BP + E$. The term BP is very small compared to E . We shall see that $B = 0.23/\sqrt{T_a}$ and have already found $E = 0.0048 \sqrt{T_a}$. Substituting these values of B , E and F in (42) and solving for T_a , we find $T_a = 810$. From this we may now calculate T_a at all other filament temperatures, as we did at the lower pressures. Thus, taking $S = 1.2$ from Table X, we calculate $\varphi_a - \varphi_1$ from the corresponding values of W in Table II. If we use these values of $\varphi_a - \varphi_1$ we obtain temperatures for T_a that are much too high. However, by empirically taking $0.26 (\varphi_a - \varphi_1)$ we find, at a filament temperature of 2700° , the value $T_a = 810$ in agreement with the calculation above. The values of T_a for other filament temperatures are obtained from the corresponding values of $0.26 (\varphi_a - \varphi_1)$. The results are recorded in Table XI.

Having thus determined T_a , it is easy to find F at other temperatures by Equations 42, 54 and the relation $B = 0.23/\sqrt{T_a}$. These results are given in the fourth column of Table XI. The values of K given in the fifth column were obtained from F and W_D by (43).

The results shown in Table XII were obtained by exactly similar methods from the data of the experiments at a pressure of 4.4 mm.

TABLE XI.

Pressure 1.1 mm.

| T_f | W_D | T_a | F | K |
|-------|-------|-------|-------|-----------------------|
| 1800 | 0.11 | 350 | 0.106 | 0.28×10^{-3} |
| 1900 | 0.24 | 360 | 0.107 | 1.45×10^{-3} |
| 2000 | 0.54 | 390 | 0.110 | 7.8×10^{-3} |
| 2100 | 0.94 | 430 | 0.113 | 25×10^{-3} |
| 2200 | 1.45 | 490 | 0.119 | 68×10^{-3} |
| 2300 | 2.22 | 560 | 0.125 | 0.19 |
| 2400 | 3.13 | 630 | 0.131 | 0.47 |
| 2500 | 4.19 | 720 | 0.137 | 1.18 |
| 2600 | 5.00 | 760 | 0.141 | 2.35 |
| 2700 | 5.7 | 810 | 0.145 | 4.7 |
| 2800 | 6.4 | 840 | 0.147 | 10.2 |
| 2900 | 7.0 | 870 | 0.149 | 33.0 |

TABLE XII.

Pressure 4.4 mm.

| T_f | W_D | T_a | F | K |
|-------|-------|-------|-------|-----------------------|
| 1800 | 0.22 | 370 | 0.155 | 0.59×10^{-3} |
| 1900 | 0.43 | 390 | 0.156 | 2.3×10^{-3} |
| 2000 | 0.71 | 420 | 0.157 | 6.3×10^{-3} |
| 2100 | 1.26 | 460 | 0.158 | 20×10^{-3} |
| 2200 | 2.10 | 520 | 0.162 | 59×10^{-3} |
| 2300 | 3.42 | 600 | 0.166 | 0.163 |
| 2400 | 4.95 | 690 | 0.172 | 0.38 |
| 2500 | 7.10 | 790 | 0.177 | 0.90 |
| 2600 | 9.80 | 900 | 0.183 | 2.10 |

8. Final Results for the Dissociation Constant K , and the Heat of Formation q_2 .

From the experiments at low pressures we have been able to calculate the numerical value of C and E and obtain preliminary estimates of B and q . From the experiments at each of the pressures up to 4.4 mm. we have calculated the dissociation constant K at temperatures from 1800 to 2900° and have collected the results in Tables IX, XI and XII. We are now in a position to test out the correctness of the theory which has been developed in this paper. The conditions which should be fulfilled by the values of K are

1. K should be independent of the pressure.
2. K should vary with the temperature according to van't Hoff's equation; that is, $\log K$ plotted against $1/T$ should give a straight line. The slope of this line determines the value of q .
3. The value of q thus found should agree with that obtained at higher pressures.

We see by examination of the tables that the values of K , found at the three higher pressures 0.207, 1.1 and 4.4 mm. are in excellent agreement. At 0.039 mm. the agreement is also good at the higher temperatures, but poorer at the lower temperatures. The results at 0.015 mm. are considerably lower than the others. On the whole, however, considering that these experiments extend over a range of pressures of nearly 300-fold, the agreement between the different values of K is surprisingly good.

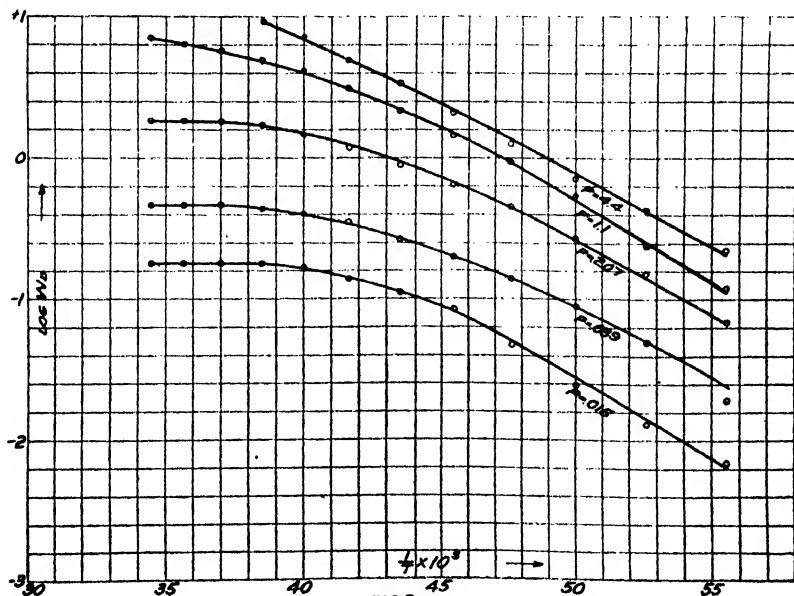
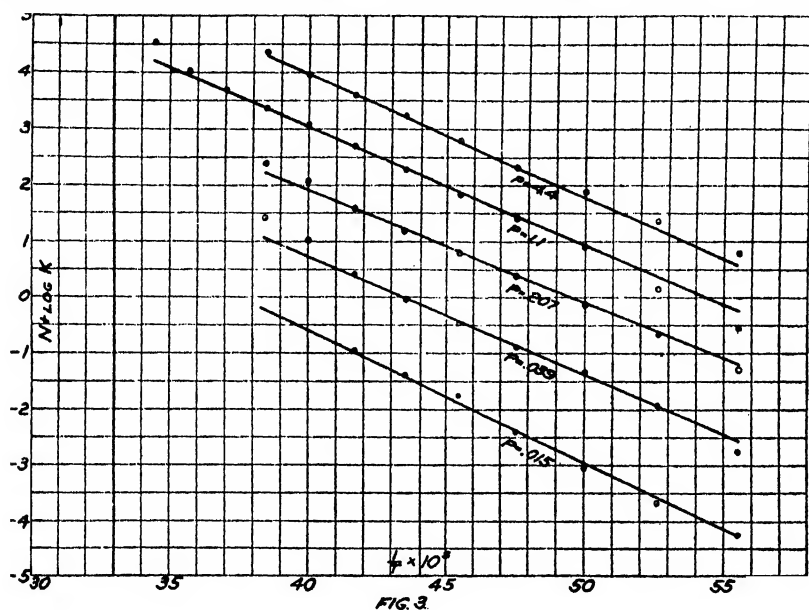


FIG. 2
EXPERIMENTS AT LOW PRESSURES

At the lowest pressures the correction for radiation from the filament is so large that errors from this cause, particularly at the lower temperatures, may perhaps account for the observed variation in K .

In Fig. 3 the values of $\log K$ have been plotted against $1/T$. In order to prevent the curves from overlapping, the successive curves have been displaced vertically by one unit; thus $\log K$ is plotted for $P = 0.015$ mm., while $(1 + \log K)$ has been plotted for $P = 0.039$ and $(2 + \log K)$ for



$P = 0.207$, etc. The curves should be parallel and equidistant straight lines. The fact that they are actually so very nearly straight and parallel is excellent evidence of the correctness of the theory, especially so, since the curves obtained by plotting W_D in a similar way (see Fig. 2) are by no means straight.

Before proceeding further we will now examine the data and choose the most probable values of q to be used in subsequent calculations.

The slope of the lines in Fig. 3 enables us to calculate q by Equation 50. The results thus obtained are given in Table XIII.

TABLE XIII.

q = Heat of Formation of Hydrogen at Constant Pressure.

| | | | | | |
|---------------|---------|--------|--------|---------|--------|
| Pressure..... | 0.015 | 0.039 | 0.207 | 1.1 | 4.4 |
| q | 108,000 | 96,000 | 91,500 | 100,000 | 97,000 |

We may also determine q from the experiments at higher pressures. For this purpose we may combine Equations 50 and 43. The difficulty arises that F is not strictly independent of the temperature, but varies

with it slightly and to an extent that depends on the relative magnitude of BP and E (see Equation 42). Since the variation of F with the temperature is small compared with that of W_D , we may proceed as follows in calculating q :

At the higher pressures now being considered, we may safely place $\sqrt{T/T_1} = 1$ in Equation 43. We shall also see that under the conditions of our experiments at higher pressures the term FW_D in the denominator of (43) can be neglected in comparison with P.

Equation 43 thus simplifies to

$$(58) \quad K = F^2 W_D^2 / P.$$

If we substitute this value of K in (50) and carry out the indicated operations, we obtain

$$(59) \quad \frac{2d \log W_D}{d(1/T)} + \frac{2d \log F}{d(1/T)} = - \frac{q}{4.57}.$$

Now it can be readily shown by taking into account Equations 42, 32 and 34 that

$$(60) \quad \frac{2d \log F}{d(1/T)} = \frac{T}{2.30} \frac{PB - E}{PB + E}.$$

This term is in the nature of a correction term. The first term of (59) is obtained directly by plotting $\log W_D$ against $1/T$. To calculate q we may therefore transform (59) to the following:

$$(61) \quad q = -9.14 \frac{d \log W_D}{d(1/T)} - 1.98 T \frac{PB - E}{PB + E}.$$

It is seen that the correction term can never exceed $1.98 T$.

Curves were prepared from the data of Table III by plotting $\log W_D$ against $1/T$. At the higher pressures these curves were very nearly straight lines. The slopes of these lines, multiplied by 9.14, gives the quantities represented by the first term of the second number of Equation 61. The values thus found are given in the second column of Table XIV.

TABLE XIV.

| Pressure. | $-9.14 \times \text{slope.}$ | $-1.98 T \frac{PB - E}{PB + E}$ | q . |
|-----------|------------------------------|---------------------------------|--------|
| 10 | +79400 | +4000 | 83400 |
| 25 | 80200 | +2000 | 82200 |
| 50 | 81000 | 0 | 81000 |
| 100 | 96200 | -2000 | 94200 |
| 200 | 107600 | -3600 | 104000 |
| 750 | 91400 | -5200 | 86200 |

To calculate the correction term, the relative values of B and E must be known. We shall see that B is equal to $0.23/\sqrt{T_a}$. If we consider that $T_a = T_2$ and thus calculate B for a mean temperature of 3000, we obtain $B = 0.005$. Similarly, we find from (54) $E = 0.26$. With these values

we may calculate the correction term corresponding to the second term of the second member of (61). The results are shown in the third column of Table XIV.

The resulting values for the heat of formation are given in the fourth column. When these are compared with the values obtained at low pressures (given in Table XIII), it is seen that the agreement is reasonably good.

Averaging all the results gives $q = 93000$. It is felt, however, that a properly weighted mean is closer to 90000. We shall therefore adopt for our final value of q .

$$(62) \quad q = 90000 \text{ calories.}$$

This is the heat of formation of 2 grams of hydrogen molecules from atoms at constant pressure and at 3000° K . At constant volume we obtain (at 3000° K)

$$(63) \quad q_2 = 84000 \text{ calories.}$$

Substituting the above value for q in (50) and integrating, neglecting the small variation of q with the temperature, we find

$$(64) \quad \log K = a - \frac{90000}{4.57T} = a - \frac{19700}{T}.$$

To determine the coefficient a we need to know the value of K at some one temperature. Let us choose 2300° as the temperature at which the low pressure results for K are most nearly free from experimental error. At higher temperatures the term FW_D in the denominator of (43) introduces some uncertainty, whereas at lower temperatures W_D becomes too small compared with W_C (see Tables II and III). By referring to Tables IX, XI, XII, we thus obtain for $T_2 = 2300$:

| | | | | | |
|---------------|-------|-------|-------|-------|-------|
| Pressure..... | 0.015 | 0.039 | 0.207 | 1.1 | 4.4 |
| K..... | 0.042 | 0.085 | 0.160 | 0.193 | 0.163 |

The mean of these is $K = 0.12$, but since the results at the lowest pressures are more subject to error a more probable value is thought to be

$$K = 0.16 \text{ at } T_2 = 2300.$$

Substituting this in (64), we find

$$a = 7.77.$$

Our final equation for the dissociation constant of hydrogen is

$$(65) \quad \log K = 7.77 - 19700/T.$$

The values of K corresponding to various values of T as calculated from this equation, are given in the second column of Table XV. From these, the corresponding degree of dissociation at atmospheric pressure and at 1 mm. pressure were calculated by solving the equation:

$$(66) \quad x^2/(1-x) = K/P$$

where x is the degree of dissociation and is equal to

$$(67) \quad x = p_1/P.$$

The results of these calculations are given in the third and fourth columns of Table XV.

TABLE XV.
Dissociation Constant K (mm. pressure) and Degree of Dissociation x .

| x . | | | | x . | | | |
|-------|-------------------------|-------------|-----------|-------|------|-------------|-----------|
| T. | K. | P = 760 mm. | P = 1 mm. | T. | K. | P = 760 mm. | P = 1 mm. |
| 1200 | 0.0023×10^{-6} | 0.000002 | 0.00005 | 2500 | 0.78 | 0.0315 | 0.575 |
| 1300 | 0.042×10^{-6} | 0.000007 | 0.0002 | 2600 | 1.55 | 0.044 | 0.692 |
| 1400 | 0.48×10^{-6} | 0.000025 | 0.0007 | 2700 | 3.0 | 0.061 | 0.79 |
| 1500 | 4.3×10^{-6} | 0.000075 | 0.0021 | 2800 | 5.4 | 0.081 | 0.86 |
| 1600 | 30.0×10^{-6} | 0.00020 | 0.0055 | 2900 | 9.3 | 0.105 | 0.91 |
| 1700 | 0.00015 | 0.00044 | 0.012 | 3000 | 16.2 | 0.13 | 0.94 |
| 1800 | 0.00066 | 0.00093 | 0.025 | 3100 | 26.0 | 0.17 | 0.96 |
| 1900 | 0.0025 | 0.0018 | 0.049 | 3200 | 42.0 | 0.21 | 0.98 |
| 2000 | 0.0083 | 0.0033 | 0.087 | 3300 | 63.0 | 0.25 | 0.985 |
| 2100 | 0.024 | 0.0056 | 0.143 | 3400 | 93.0 | 0.29 | 0.989 |
| 2200 | 0.065 | 0.0092 | 0.224 | 3500 | 138 | 0.34 | 0.993 |
| 2300 | 0.16 | 0.0145 | 0.328 | 4000 | 710 | 0.61 | 0.999 |
| 2400 | 0.36 | 0.0216 | 0.447 | | | | |

9. Test of the Theory.

By examining Equations 31 to 34, we see that, by a knowledge of the values of K , q , T_a , B , C , and E , we should be able to calculate W_D for any temperature and pressure. By comparing the results of these calculations with the observations (Table III), we are enabled to test the validity of the assumptions made.

Before making such calculations it is necessary to determine the numerical value of the coefficient B . We have already seen that the maximum value of W_D which we have denoted by W_{\max} , is not subject to error through the uncertainty in the actual pressures within the bulb. Equation 44 is therefore particularly well adapted for the calculation of B .

By substituting the values of W_{\max} from Table VIII in Equation 44, together with the corresponding values of K and E and solving the resulting equations for B , the average result is found to be

$$(68) \quad B = 0.23/\sqrt{T_a}.$$

As a test of the theory from which (44) was derived, we may now employ this value of B to calculate W_{\max} , and by Equation 45 to calculate P' , using the values of K from Table XV and the values of E given by (54). For these calculations T_a was taken equal to T_b , since the pressures at which W_D reaches a maximum are so high that this must be approximately true. Moreover, the value of W_{\max} is only dependent on T_a to a very slight degree.

TABLE XVI.

| T. | $W_{\max.}$ | | P' | |
|------|-------------|-----------|-------------|-----------|
| | Calculated. | Observed. | Calculated. | Observed. |
| 2000 | 1.36 | 1.4 | 43 | 25 |
| 2200 | 3.85 | 4.0 | 48 | 50 |
| 2400 | 8.62 | 8.9 | 54 | 50 |
| 2600 | 17.6 | 16.7 | 63 | 50 |
| 2800 | 30.4 | 30.0 | 76 | 50 |
| 3000 | 48.3 | 48.0 | 94 | 50 |
| 3200 | 69.4 | 75.0 | 120 | 100 |
| 3400 | 92.5 | 117.0 | 152 | 100 |

The calculated values of $W_{\max.}$ and P' thus obtained are placed in Table XVI side by side with the experimentally found figures.

The agreement in the values of $W_{\max.}$ is surprisingly good, especially when it is remembered that the values of K and E , which were used in the calculation, were obtained solely from the experiments at low pressures. The closeness of the agreement over such a wide range of temperature is strong evidence of the correctness of the value of q that was adopted in calculating K .

The discrepancy at the highest temperatures may be explained, I think, as being due to experimental errors caused by electrical leakage through the gas. This effect was noticed strongly at the highest temperatures in the experiment at 4.4 mm. pressure. In this case the discharge through the gas entirely prevented measurements above about 2800°, since the voltage actually decreased as the current was raised. Since the resistance was observed in all cases it was possible to show that this effect was not very serious in the other experiments. It is possible, however, that this effect in an incipient stage may have slightly increased the values of W_D at the highest temperatures, at pressures below 200 mm.

In future experiments this effect could be avoided by using wires of larger diameter so that the potential drop along the wire would be insufficient to ionize the gas.

The agreement between the calculated and observed values of P' in Table XVI is also satisfactory. The calculated gradual increase in P' with increasing temperature is in full accord with the observations.

It must be remembered that the observed pressures were those at which the bulbs were sealed off and that the actual pressures in the bulbs while the filaments were heated must have been much higher. The fact that the calculated values are larger than the observed therefore adds support to the theory.

The value of B obtained above, (68), enables us to calculate the diffusion coefficient D by Equation 32. The shape factor S which is involved in this equation may be calculated from (7), taking $d = 0.00706$ cm. and $b = 3.7$ cm. (see Table V). This gives $S = 1.01$. By substituting this

in (32), together with $q_1 = 42000$ and the value of B from (68), we find

$$(69) \quad D_0 = 9.6 \text{ cm}^2. \text{ per sec.}$$

This is the value of the diffusion coefficient at 0° C. as obtained by extrapolation downwards from high temperatures by Equation 29. At higher temperatures and at atmospheric pressure, we thus obtain from the same equation, together with (69):

$$(70) \quad D = 2.14 \times 10^{-3} T^{5/2}$$

In the "paper of 1912" D was calculated to be equal to

$$(71) \quad D = \frac{0.514 \times 10^{-3} T^{5/2}}{1 + 77/T}$$

This result was obtained, according to the kinetic theory, on the assumption that the free path of hydrogen atoms and hydrogen molecules are the same. At high temperatures the second term in the denominator of (71) becomes negligible and we thus see that the present results show that the diffusion coefficient of hydrogen atoms through molecular hydrogen is 4.2 times as great as had been previously calculated.

A very thorough test of the theory is afforded by a comparison of the values of W_D calculated according to the theory, with those determined experimentally. In Tables XVII and XVIII the observed and calculated

TABLE XVII.
Comparison of Observed and Calculated Values of W_D .
Low Pressures.

| T ₁ | P = 0.015 mm. W_D | | P = 0.039 mm. W_D | | P = 0.207 mm. W_D | | P = 1.1 mm. W_D | | P = 4.4 mm. W_D | |
|----------------|------------------------|-------|------------------------|-------|------------------------|-------|----------------------|------|----------------------|------|
| | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. |
| 1800 | 0.007 | 0.022 | 0.019 | 0.037 | 0.068 | 0.083 | 0.11 | 0.17 | 0.22 | 0.24 |
| 2000 | 0.025 | 0.066 | 0.09 | 0.116 | 0.27 | 0.27 | 0.54 | 0.58 | 0.71 | 0.85 |
| 2200 | 0.085 | 0.124 | 0.20 | 0.25 | 0.65 | 0.64 | 1.45 | 1.44 | 2.10 | 2.31 |
| 2400 | 0.139 | 0.162 | 0.35 | 0.38 | 1.17 | 1.12 | 3.13 | 2.82 | 4.95 | 4.95 |
| 2600 | 0.179 | 0.176 | 0.45 | 0.44 | 1.71 | 1.49 | 5.00 | 4.4 | 9.8 | 9.0 |
| 2800 | 0.180 | 0.179 | 0.47 | 0.46 | 1.85 | 1.69 | 6.4 | 5.8 | | |

TABLE XVIII.
Comparison of Observed and Calculated Values of W_D .
Higher Pressures.

| T ₁ | P = 10 mm. | | P = 25. | | P = 50. | | P = 100. | | P = 200. | | P = 750. | |
|----------------|------------|------|---------|------|---------|------|----------|------|----------|------|----------|------|
| | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. |
| 1800 | ... | 0.31 | 0.41 | 0.38 | ... | 0.38 | 0.33 | 0.35 | 0.23 | 0.28 | 0.19 | 0.17 |
| 2000 | 1.0 | 1.02 | 1.3 | 1.3 | ... | 1.35 | 1.1 | 1.3 | 0.67 | 1.04 | 0.64 | 0.62 |
| 2200 | 2.7 | 2.8 | 3.2 | 3.6 | 4.0 | 3.8 | 2.8 | 3.5 | 1.70 | 2.98 | 1.8 | 1.8 |
| 2400 | 5.8 | 6.1 | 7.1 | 8.1 | 8.9 | 8.7 | 6.5 | 8.2 | 4.0 | 7.1 | 4.2 | 4.4 |
| 2600 | 10.8 | 11.2 | 13.5 | 15.4 | 16.7 | 17.2 | 12.5 | 16.7 | 9.0 | 14.6 | 8.8 | 9.2 |
| 2800 | 19.3 | 17.2 | 24.0 | 25.2 | 30.0 | 29.7 | 25.0 | 30.0 | 20.0 | 27.0 | 17.0 | 17.3 |
| 3000 | 30.0 | 23.0 | 38.6 | 37.0 | 48.0 | 45.5 | 45.0 | 48.5 | 40.0 | 44.9 | 29.0 | 30.0 |
| 3200 | 46.0 | 26.5 | 58.0 | 47.2 | 74.0 | 62.0 | 75.0 | 69.3 | 68.0 | 67.0 | 47 | 47.5 |
| 3400 | | 29.0 | | 54.0 | 107 | 75.5 | 117 | 90.3 | 97.0 | 91.0 | 69 | 70.7 |

values have been placed side by side. The "observed" values are taken directly from Table III of Part I. The calculated values were obtained by solving Equation 43 for W_D after substituting it in the numerical values of K , F , T_a and T_2 .

For this purpose the values of K were taken from Table XV, which was obtained directly from Equation 65. At 0.015 and 0.039 mm. pressure T_a was taken to be 300°K. , whereas at pressures from 0.207 to 4.4 mm. the values of T_a used in the calculations were those given in Tables IX, XI and XII. At pressures of 10 mm. and more, T_a was taken equal to T_2 . The coefficient F was calculated for each temperature and pressure by substituting the values of B and E from (68) and (54) into Equation 42.

The values of W_D have thus been calculated directly from the dissociation constant, the diffusion coefficient, and the coefficients α_1 and α_2 . An examination of Tables XVII and XVIII shows that the agreement is on the whole excellent; so good, in fact, that it would seem to show not only that we are dealing with a real dissociation of hydrogen into atoms, but that our theory of the mechanism of the process is substantially correct.

10. General Discussion.

The theory which has been used in the present paper was only developed after several attempts had been made to calculate the degree of dissociation by other methods. Each of these other methods, however, seemed to lead to conclusions which could only be reconciled with the experimental data by making many improbable and arbitrary assumptions. These difficulties disappear, however, when we adopt the present theory of the mechanism of the reaction. A brief discussion of the unsuccessful hypotheses will enable us to see that they are untenable.

In attempting to analyze the probable mechanism of the reaction, three possibilities suggest themselves:

1. The dissociation occurs in the heated gas around the wire.
2. The dissociation occurs *on the surface* of the wire by the impact of the molecules and atoms against the surface.
3. The dissociation occurs in the wire or in a surface layer where equilibrium prevails.

The first hypothesis assumes that the tungsten does not act catalytically on the reaction, and is therefore in itself very improbable. Moreover, it leads to conclusions irreconcilable with the experiments at low pressures, where, in a sense, there is no heated gas around the wire.

The second hypothesis seemed at first sight to have much in its favor, and by its aid it was possible to estimate an upper and lower limit to the degree of dissociation.

Whatever the mechanism of the reaction on, or in, the wire, it was possible to analyze the process as follows:

Let ϵ_2 represent, out of all the hydrogen molecules which strike the

wire, that fraction which becomes dissociated into atoms. Similarly, ϵ_1 represents, out of all the atoms that strike the wire, that fraction which recombines to form molecules. We may consider that the reaction actually observed is simply the difference between these opposite reactions. It is clear that neither ϵ_1 nor ϵ_2 can ever exceed unity.

For further progress, it is necessary to make some assumptions regarding these coefficients. It is evident that either ϵ_1 or ϵ_2 or both must vary with the temperature. The simplest assumption is that they are independent of the pressure. By applying Equation 5 we then readily find that the condition for equilibrium is

$$p'_1 = \sqrt{2} (\epsilon_2/\epsilon_1) p'_2.$$

Since ϵ_1 cannot exceed unity, this gives us a lower limit for the degree of dissociation, provided we can estimate ϵ_2 . By assuming a value for the heat of reaction it is possible to calculate ϵ_2 from W_D by an equation similar to (16). In this way it was concluded that the degree of dissociation at 3200° K. and atmospheric pressure must exceed 5%.¹

In order, however, to account for the manner in which W_D had been observed to vary with temperature and pressure, it was necessary that ϵ_2 should increase with the temperature up to a limiting value of 0.68, but at the same time should decrease in a complicated way as the pressure increased. Similarly, ϵ_1 would have to increase with the pressure and decrease with increasing temperature. This theory gave no clue as to the cause of the variations of ϵ_1 and ϵ_2 .

The fact that ϵ_1 and ϵ_2 were found to be such complicated functions of both temperature and pressure suggested the third hypothesis; namely, that the reaction does not occur at the surface, but that there is an actual equilibrium in the wire which determines the velocity of the reaction. This view was strengthened by the fact that ϵ_1 and ϵ_2 varied with the temperature and pressure in the way that would be expected of the partial pressures of two gases in equilibrium.

On the basis of the third hypothesis, the coefficients ϵ_1 and ϵ_2 lose their fundamental significance, while the coefficients α_1 and α_2 take their place. The fact that the latter coefficients prove to be constant and practically equal to unity over such wide ranges of temperature and pressure is excellent evidence that, in the present theory, we are dealing with the factors that fundamentally determine the velocity of the reaction.

By means of our present theory we are enabled to calculate ϵ_1 and ϵ_2 at any temperature and pressure.

Let us consider the case that hydrogen molecules at pressure p_2 strike the wire, but that the hydrogen atoms formed do not again return to the wire. Then $\epsilon_2 m_2$ represents the rate of formation of atomic hydrogen.

¹ Table XV gives 21%.

This, however, is equal to the quantity we have called ω (see Equation 17): thus,

$$(72) \quad \omega_2 = \epsilon_2 m_2.$$

Substituting this, together with the value of m_2 (by Equation 5) in (26), we obtain, after placing $\alpha_1 = \sqrt{2} \alpha_2 = 1$

$$(73) \quad K = \sqrt{\frac{T_2}{T_a}} \frac{2 p_2 \epsilon_2^2}{1 - \sqrt{2} \epsilon_2}$$

This equation shows clearly that at low temperatures, where K is small, ϵ_2 is inversely proportional to $\sqrt{p_2}$, whereas at higher temperatures it approaches a limiting value of 0.71. Thus the variation of ϵ_2 with the temperature and pressure which it was necessary to assume when working with the second hypothesis, receives a complete explanation by the third hypothesis.

In a similar way, the value of ϵ_1 may be calculated for the case that the wire is surrounded by atomic hydrogen, while the partial pressure of molecular hydrogen is zero. In this case

$$(74) \quad \omega_1 = - \epsilon_1 m_1$$

and we thus find, from (26)

$$(75) \quad K = \sqrt{\frac{T_2}{T_a}} \frac{(1 - \epsilon_1)^2 p_1}{\epsilon_1}.$$

This shows that at low temperatures ϵ_1 must be constant and equal to unity, whereas at high temperatures it decreases and becomes proportional to the pressure. Thus again, the third hypothesis offers a simple explanation of the difficulty encountered in applying the second hypothesis.

It is evident that ϵ_1 and ϵ_2 completely lose their significance when both hydrogen molecules and atoms are present around the wire. We cannot profitably look upon the reaction as being the difference between two opposing reactions taking place *upon the surface*.

In fact, the velocity of the reaction does not follow Gulberg and Waage's Mass Law in the ordinary sense. Neither do diffusion phenomena (at least at low pressures) seem to have any effect on the reaction velocity. The velocity is determined simply by the rate at which the molecules and atoms strike the surface of the wire and the *equilibrium concentrations* of atomic and molecular hydrogen within the wire.

Effect of Bulb Temperature.—In studying chemical reactions at low pressures it has been pointed out¹ that the temperature of the filament and that of the gas molecules striking it can be varied independently of one another. By changing the bulb temperature, the velocity (and internal energy) of the hydrogen molecules striking the filament can be varied over a wide range. If the reaction takes place entirely on the surface in accordance with the second hypothesis, we should expect that the

¹ Langmuir, *THIS JOURNAL*, 35, 105 (1913).

relative velocities of the hydrogen molecules and the tungsten atoms with which they collide, would determine the velocity of the reaction. Because of the small mass of the hydrogen molecules it happens that the average velocity of hydrogen molecules at room temperature or even liquid air temperatures, is much greater than that of tungsten atoms at 3500° . Therefore, the amount of impact between the hydrogen molecules and tungsten atoms depends vastly more on the bulb temperature than it does on the temperature of the filament. In case the impact determines the reaction velocity, we see that the latter should be greatly affected by bulb temperature.

On the other hand, if the reaction takes place in the metal in accord with the third hypothesis, we should not expect the bulb temperature to materially affect the velocity of the reaction. It is to be expected, however, that the bulb temperature might have a slight effect on the coefficient α_2 and thus slightly change the velocity of the reaction.

Some experiments were undertaken to determine whether cooling the bulb in liquid air had any effect on the values of W_D obtained at low pressures (from 0.01 to 0.1 mm.). The results showed conclusively that the bulb temperature was without material effect on the velocity of the reaction. This fact affords additional evidence that the velocity depends primarily on some equilibrium condition within the surface of the wire.

Specific Heat of Hydrogen at High Temperatures.—When hydrogen is heated to a temperature at which appreciable dissociation occurs, the heat absorbed by the reaction may be very large compared with that which would be required if there were no dissociation. We should therefore expect a very large increase in the apparent specific heat of hydrogen at very high temperatures. In Part I we have already briefly discussed Pier and Bjerrum's experiments on the specific heat of hydrogen by the explosion method. We saw that the earlier calculations of the dissociation of hydrogen (paper of 1912) led to apparent specific heats too high to reconcile with the results of the explosion method, unless we assumed that equilibrium was not reached during the short period of the explosion.

In order to compare our present results with the data of the explosion method, we shall calculate the increase in apparent specific heat caused by the dissociation as given in Table XV.

If we heat a gram molecule of hydrogen from 0° K. to T , the number of gram molecules of hydrogen dissociated will be $x/(2-x)$ where x is the degree of dissociation at the temperature T , x being expressed in terms of partial pressures according to (67).

The heat absorbed by this dissociation will be

$$q_2 \, x/(2-x).$$

In comparison with this we may neglect the increase in specific heat

due to the difference in the specific heat of the molecular hydrogen and that of the atomic hydrogen formed (2×2.98).

Pier¹ gives for the *mean* specific heat of hydrogen from room temperature up to $t^\circ \text{C}$.

$$C_v = 4.70 + 0.00045t$$

or in absolute temperatures

$$C_v = 4.578 + 0.00045T$$

The dissociation at higher temperatures would cause an increase in this mean specific heat amounting to

$$\frac{q_2}{T - 273} \cdot \frac{x}{(2 - x)}$$

In Table XIX are given the mean specific heats for a few temperatures, as calculated from Pier's formula, together with those calculated by taking into account the increase due to dissociation. For this calculation the values of x were taken from Table XV and q_2 was taken to be 84000 calories.

TABLE XIX.

| T. | C_v Pier. | Apparent C_v (considering dissociation). | Ratio. |
|------|----------------|---|--------|
| 1600 | 5.30 | 5.306 | .0012 |
| 1800 | 5.39 | 5.41 | .0047 |
| 2000 | 5.48 | 5.56 | .015 |
| 2200 | 5.57 | 5.77 | .036 |
| 2400 | 5.66 | 6.09 | .078 |
| 2600 | 5.75 | 6.56 | .14 |
| 2800 | 5.84 | 7.25 | .24 |
| 3000 | 5.93 | 8.09 | .36 |
| 3200 | 6.02 | 9.40 | .56 |

Siegel, in a recent paper,² discusses in detail the errors of the explosion method. He points out that, owing to a faulty method of calculation, the temperatures given by Bjerrum are considerably too high, in some cases as much as 400° . He then shows that Bjerrum's experiments exhibit certain discrepancies which could be readily explained by assuming a dissociation of the hydrogen. He then says (pages 649-50):

"In order to reconcile Langmuir's results with those of the explosion method, one must assume that in the calculations thus far, the capacity of the system (in the explosion chamber), that is, $\text{CH}_2\text{O} + \text{MCH}_3$, has been taken about 30% too high.

"Such an assumption is impossible. However, if we take for the heat of dissociation of hydrogen, the value 140000 calories instead of the 131000 calories given by Langmuir, we then find by the Nernst approximation formula:

$$\log K = Q/4.57 T + \Sigma \nu \cdot 1.75 \log T + \Sigma \nu C$$

that at 2850° and atmospheric pressure the dissociation is about 11%, which is the value given by Langmuir for 2700° . With this assumption it can be shown that the heat

¹ *Z. Elektrochem.*, 15, 536 (1909).

² *Z. phys. Chem.*, 87, 641 (1914).

cap. by the explosion experiments is 12% less than that previously taken. This result is in good agreement with the explosion method. However, I am of the opinion that the heat of dissociation should be at least 150000 calories. On the other hand, it should be emphasized that from my experiments it is not possible to determine with certainty whether or not hydrogen is dissociated at all. And—what is here very significant—by the assumption of such a dissociation, the observed anomalies in the heat losses do not find a sufficient explanation, for the anomalies also occur even at temperatures as low as 2300–2400°, where surely the dissociation of hydrogen can play no part."

Thus, according to Siegel, a dissociation as large as 11% at 2850° can be reconciled with the explosion experiments. If we refer to Table XV we see that we have found the dissociation at 2850° to be 9.2% at atmospheric pressure. This should be ample to account for the anomalies found by Siegel.

Siegel's objection that the dissociation of hydrogen could not account for the discrepancies observed at 2300–2400°, fails to apply to the present results. Siegel does not state his reasons for believing that the heat of dissociation is at least 150000 calories. Such a high value is at complete variance with all the experiments described in the present paper. With the value 84000 calories which we have adopted, the dissociation does not fall off nearly so rapidly at lower temperatures. This is readily seen from the following table:

| T. | Siegel. q = 150000. | | Langmuir. q = 84000. | |
|------|------------------------|-------|-------------------------|-------|
| | x. | ΔC/C. | x. | ΔC/C. |
| 2850 | 0.11 | 13.0% | 0.092 | 11.0% |
| 2300 | 0.0049 | 0.9% | 0.014 | 2.6% |

The figures in the second column represent the degree of dissociation calculated from Siegel's data, while those in the fourth column are taken from Table XV. The third and fifth columns give the increase in the "heat capacity of the system" $H_2O + MH_2$ referred to by Siegel. Thus, Siegel calculates that 11% dissociation at 2850° would increase the capacity by 13%. The other figures were obtained from this by proportion, taking into account, however, the effect of the temperature as was done in the preparation of Table XIX.

Thus, on Siegel's assumption of a high heat of dissociation, the effect of the dissociation is to increase the heat capacity at 2850° by 13%, but only by 0.9% at 2300°. It is evidently for this reason that he says that "surely the dissociation can play no part" at such low temperatures as 2300°.

Taking the values for the dissociation as calculated in the present paper, we find that the heat capacity would be increased 11% at 2850 and 2.6% at 2300°, an amount probably sufficient to account for the anomalies found by Siegel.

Thus, the explosion method gives additional evidence for the dissociation of hydrogen and confirms the substantial accuracy of the results.

II. Rate of Formation of Active Hydrogen.

It has been shown¹ that the disappearance of hydrogen in contact with a heated filament is caused by the deposition of atomic hydrogen on the bulb.

The present theory enables us to calculate the rate at which atomic hydrogen should be formed in contact with a tungsten wire. The rate at which atomic hydrogen is deposited on the bulb should naturally be less than that at which it is formed by the wire.

In the paper referred to, it was stated that the disappearance of hydrogen "was often quite marked when the wire was at a temperature as low as 1300° K.," but very few quantitative data at such low temperatures were given. By looking through the original notes of these experiments, I find that at low temperatures the highest rates of disappearance were as follows:

Experiment 160. Filament temperature 1200° K. In seven minutes the pressure fell from 16.4 to 15.6 microns, although at 1100° K. no decrease in pressure could be observed. The surface of the filament was 0.15 sq. cm. The rate of disappearance was 1.4 cubic millimeters of H₂ per minute per sq. cm. of surface.

Experiment 173. With the filament at 1270° the pressure decreased from 16.2 to 15.0 microns in three minutes. The surface of the filament was the same as before. This corresponds to a rate of 3.7 cubic mm. per minute per sq. cm.

In each case the hydrogen continued to disappear at a gradually decreasing rate for a half-hour or more. Because of this fatigue effect we shall here consider only the initial rates.

Let us now calculate the rate at which atomic hydrogen should have been produced by wires at these temperatures. In Equation 26 we may place $p_1 = 0$; $p_2 = P$ and may neglect the second term of the denominator at these low pressures and temperatures. Since the factor $\sqrt{2\pi R}$ is equal to 17.15 and α_1 is unity, we thus obtain

$$(76) \quad K = 325. \sqrt{T_0 T_1} \omega^2 / P.$$

In this equation ω is the rate of dissociation of hydrogen in grams per second per sq. cm. of filament surface. Let R be the rate of dissociation of molecular hydrogen in cubic mm. per sq. cm. per minute. We then have

$$(77) \quad R = 7.2 \times 10^8 \omega$$

whence from (76), by placing $T_0 = 300$

$$(78) \quad R = 9.6 \times 10^6 \sqrt{KP} T^{-1/2}.$$

¹ THIS JOURNAL, 34, 1310 (1912).

Substituting in this the values of R from Table I, and taking the values of P and T given above, we obtain the values given below as "R cal." For comparison these are placed side by side with those found by experiment.

| | T. | R calc. | R obs. |
|----------------|------|---------|--------|
| Expt. 160..... | 1200 | 9.8 | 1.4 |
| Expt. 173..... | 1270 | 27.4 | 3.7 |

These results indicate that under the most favorable conditions realized in the experiment, only about one-seventh of the hydrogen dissociated was deposited as "active hydrogen" on the bulb. In the great majority of cases the fatigue effect made the observed rate of clean-up much slower.

The fact that the observed rates are less than the calculated, yet of the same order of magnitude, is a satisfactory confirmation of the theory that the disappearance and activation of hydrogen are caused by its dissociation into atoms.

There is thus quantitative evidence of the dissociation of hydrogen over the whole range of temperature from 1200° to 3500° . The substantial agreement of the calculated and observed results over such a wide range proves that the value we have found for the heat of dissociation, namely, 84000 calories, cannot be far from correct.¹

12. Experiments with Mixtures of Hydrogen and Nitrogen.

Some experiments have been made to determine the heat losses from tungsten wires in mixtures of nitrogen and hydrogen. The wire was the same as that previously used in the experiments with hydrogen. The bulbs, after being exhausted in the usual way, were filled with the mixture of gases, the *total* pressure in each case being 600 mm. Mixtures containing 1.25, 3.0, 10.0 and 30% of hydrogen were used. The results given in Table XX were obtained by subtracting from the observed watts per centimeter, the energy radiated (W_R). These figures are directly comparable with those given in Table I of Part I.

TABLE XX.

| Diam. of wire 0.00706 cm. | | Total pressure 600 mm. | | | | | |
|---------------------------|---------|-----------------------------------|----------------|----------------|-----------------|---------------------|---------------------|
| T. | W_R . | Watts per cm. carried by mixture. | | | | W_C in N_2 . | W_C in H_2 . |
| | | $p_0 = 7.5$ mm. | $p_0 = 18$ mm. | $p_0 = 60$ mm. | $p_0 = 180$ mm. | $S = 1.36$. | $S = 1.18$. |
| 1800 | 0.38 | 1.45 | 1.52 | 2.06 | ... | 1.40 | 7.4 |
| 2000 | 0.65 | 1.75 | 1.85 | 2.40 | ... | 1.70 | 9.0 |
| 2200 | 1.06 | 2.10 | 2.30 | 2.86 | 4.5 | 2.02 | 10.7 |
| 2400 | 1.60 | 2.60 | 2.95 | 3.70 | 5.8 | 2.36 | 12.6 |
| 2600 | 2.33 | 3.35 | 3.70 | 4.92 | 7.9 | 2.75 | 14.5 |
| 2800 | 3.30 | 4.23 | 4.70 | 6.78 | 11.4 | 3.14 | 16.8 |
| 3000 | 4.46 | 5.15 | 6.20 | 9.30 | ... | 3.58 | 19.1 |

¹ For example, it now becomes impossible to reconcile our experiments with the value $q_2 = 63000$ calculated according to the method of Bohr, *Phil. Mag.*, 26, 863 (1913); 27, 188 (1914).

TABLE XXI.

Observed and Calculated Values of W_D .

| T. | $p_0 = 7.5$ mm. | | $p_0 = 18$ mm. | | $p_0 = 60$ mm. | | $p_0 = 180$ mm. | |
|------|-----------------|------|----------------|------|----------------|------|-----------------|------|
| | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. | Obs. | Cal. |
| 1800 | -0.01 | | -0.03 | | +0.08 | | ... | ... |
| 2000 | +0.06 | 0.03 | -0.05 | 0.04 | 0.00 | 0.08 | ... | ... |
| 2200 | 0.00 | 0.08 | +0.05 | 0.13 | 0.00 | 0.24 | -0.1 | 0.4 |
| 2400 | +0.15 | 0.20 | +0.33 | 0.32 | 0.36 | 0.60 | +0.4 | 1.0 |
| 2600 | 0.45 | 0.41 | 0.60 | 0.65 | 1.00 | 1.23 | 1.6 | 2.2 |
| 2800 | 0.93 | 0.72 | 1.18 | 1.20 | 2.30 | 2.30 | 4.2 | 4.2 |
| 3000 | 1.37 | 1.10 | 2.20 | 1.92 | 4.18 | 3.96 | ... | ... |

To obtain the heat carried from the wire by the dissociation, it is necessary to subtract W_C . In the last two columns of Table XX are the calculated values of W_C for pure nitrogen and hydrogen at pressures of 600 mm. These are obtained by multiplying S by the values of $\varphi_2 - \varphi_1$ given in Tables III and IV. For the mixture of hydrogen and nitrogen W_C was found by interpolating linearly between the values calculated for the pure gases. By subtracting these results from the watts per cm. of Table XX the values of W_D given in Table XXI as "cal." were obtained. The smallness of the differences at lower temperatures shows that the heat carried by convection in mixtures of gases is approximately an additive function of the partial pressures (the total pressure remaining constant).

To calculate the values of W_D for mixtures of gases according to our theory we need to start from Equation 27. From this we can eliminate p_1 and p_2 as before, by means of Equation 30. The significance of P and p_2 , however, is now somewhat different, so we must proceed from this point in a slightly different way. In Equation 30, P is the total pressure, and p_1 the partial pressure of atomic hydrogen. We then have

$$(79) \quad p_2 = p_0 - \frac{1}{2}p_1$$

where p_0 is the partial pressure of molecular hydrogen before dissociation occurs and p_2 is the partial pressure of molecular hydrogen after dissociation.

In the present case we may place $T_0 = T_2$; $P = 600$, $S = 1.34$, and $q_1 = 42000$. From (30) we thus find

$$(80) \quad p_1 = 946W_D / (D_0\sqrt{T}).$$

Combining (79) and (80) with (27), we find

$$(81) \quad K = \frac{W_D^2 (946/D_0\sqrt{T} + E)^2}{p_0 - W_D (473/D_0\sqrt{T} + E)}$$

where E is given by (34).

By trial it was found that (81) gives the best agreement between the observed and calculated values of W_D if D_0 is placed equal to 2.5.

Calculating E by (54) it is evident that E is negligible compared to

$473/2.5\sqrt{T}$ over the whole range of temperatures covered by the experiments. Equation 81 thus simplifies to

$$(82) \quad W_D = \sqrt{\frac{K p_0 T}{144000}} \times \sqrt{1 - \frac{190}{p_0 \sqrt{T}}} W_D.$$

This quadratic equation can be conveniently solved for W_D by using a series of approximations, since the second radical is always close to unity. In this way, by taking K from Table XV, the values of W_D for different temperatures and partial pressures have been calculated. The results are placed side by side with the observed values in Table XXI.

The agreement is entirely satisfactory, considering the crudeness of some of the assumptions made.

The theory receives additional confirmation through the fact that the observed values of W_D increase in proportion to the square root of the partial pressure as demanded by the theory, whereas at lower temperatures the observed values of W_C increase linearly with the partial pressure.

From the value of D_0 we may conclude by (29) that the diffusion coefficient of hydrogen atoms through nitrogen at high temperatures and atmospheric pressure is

$$(83) \quad D = 2.5 (T_a/273)^{1/2}.$$

Comparing this with (69) we see that the ratio of the diffusion coefficient of hydrogen atoms through hydrogen to that through nitrogen is $9.6/2.5 = 3.84$.

If we calculate the free path of hydrogen atoms through nitrogen according to the principles of the kinetic theory, using Equations 20 and 21 on page 865 of the "paper of 1912," we obtain

$$(84) \quad D_{\text{cal.}} = 2.16 (T/273)^{1/2}.$$

This agrees well with the diffusion coefficient calculated from the experiments (Equation 83). We have previously remarked that the observed rate of diffusion of hydrogen atoms through molecular hydrogen was found to be 4.2 times greater than that calculated. Evidently hydrogen atoms behave abnormally when diffusing through molecular hydrogen, but not when diffusing through nitrogen. This is probably caused by the hydrogen atoms going, we might say, through the hydrogen molecules by combining with one atom in a molecule with which it collides and thus liberating the other. This effect is probably entirely analogous to the abnormal mobility of the H and OH ions in aqueous solutions.

13. Summary.

1. Previous calculations of the degree of dissociation of hydrogen, from experiments on the heat losses from tungsten wires in hydrogen, conflicted rather seriously with Bjerrum's determinations of the specific heat of hydrogen by the explosion method. The weak point in the method

of calculation was a rather arbitrary assumption regarding the diffusion coefficient of atomic hydrogen through ordinary hydrogen.

2. This apparent discrepancy suggested that the actual amount of dissociation might be somewhat less than that previously calculated, but did not indicate that the abnormal heat conductivity of hydrogen at high temperatures was not due to dissociation.

3. The qualitative evidence of such a dissociation seems conclusive. Thus, not only does hydrogen show an entirely abnormal increase in heat conductivity, but this heat conductivity actually increases as the pressure is lowered.

A large amount of chemical evidence has also been accumulated. If hydrogen at low pressures comes into contact with metallic wires at temperatures above 1300° K., part of the hydrogen is converted into an active modification which remains adsorbed on glass surfaces for long periods of time. This active hydrogen can react at room temperature with oxygen or with many reducible substances, or can dissolve in metals such as platinum. There are good reasons for thinking that this active hydrogen is hydrogen in the atomic condition.

4. A series of experiments were made to measure, more accurately than hitherto, the heat losses from a tungsten wire at temperatures from 800° to 3500° K. and at pressures of hydrogen ranging from 0.01 mm. up to atmospheric pressure. Similar experiments were made with nitrogen.

5. At temperatures below that at which dissociation occurs the heat loss from the wires decreases steadily as the pressure is lowered. Only at pressures above 200 mm. do convection currents play any important part. Below this pressure the decrease in the heat loss is due to the temperature discontinuity, first observed by Smoluchowski. The theory of this effect is developed for the case of small wires at very high temperatures and the results are found to be in good agreement with the experiments.

6. The normal heat conductivity is separated from the abnormal effect due to dissociation, and a table is prepared (Table III) giving the heat carried from the wire by the dissociation, at various temperatures and pressures. With nitrogen there is no abnormal increase in heat loss at high temperatures.

7. The following theory of the phenomena occurring in and around the wire is proposed:

The dissociation of the hydrogen does not occur in the space around the wire, nor by the impact of molecules against its surface, but takes place only among the hydrogen molecules which have been absorbed (dissolved?) by the metal of the wire. Within the metal the reaction occurs so rapidly that equilibrium may be assumed to prevail at all times.

The equilibrium constant within the metal may, however, be very different from that in the gas phase.

It is assumed that there is no "adsorption film" on the surface of the wire through which the hydrogen has to diffuse, but that the absorption takes place by the collision of the molecules (or atoms) against the surface of the wire. A certain proportion of the molecules striking the surface may be reflected without absorption. Thus, of all the hydrogen molecules striking against the surface, we assume that a certain fraction α_2 is absorbed, while the fraction $1 - \alpha_2$ is reflected. Similarly, of all the hydrogen atoms striking the surface, the fraction α_1 is absorbed.

In general, the partial pressures of atomic hydrogen in the gas immediately surrounding the wire will not be that corresponding to the equilibrium at the temperature of the wire. The difference between these two partial pressures may be looked upon as a "drop in concentration" at the surface of the wire strictly analogous to Smoluchowski's "temperature drop" in the case of heat conduction and to Kundt and Warburg's "slip" in the case of experiments on the viscosity of gases.

The partial pressure of atomic hydrogen immediately around the wire depends on: 1st, the rate at which atomic hydrogen escapes from the wire; 2nd, the rate at which atomic hydrogen is absorbed by the wire; and 3rd, the rate at which it can diffuse away from the wire.

8. From the viewpoint of this theory it has been possible, by thermodynamical reasoning, to develop a quantitative theory by which the dissociation constant K (in the gas phase) may be calculated in terms of W_D the heat carried from the filament by dissociation; q_1 the heat of reaction; D the diffusion coefficient, and the two coefficients α_1 and α_2 .

The resulting general Equation 31 is of the form (neglecting constant factors)

$$K = \frac{(W/q)^2 (P/D + 1/\alpha_1)^2}{P - (W/q) (P/D + 1/\alpha_2)}$$

where P is the total pressure.

9. By comparing this equation with the experimental data, it is found possible to so choose the quantities K , q , D , α_1 and α_2 that the resulting equation agrees excellently with the experiments at all temperatures and pressures. At the same time, the values of K conform to the thermodynamical requirement given by van't Hoff's equation

$$d \ln K/dT = q/RT^2.$$

The agreement between the theory and the experiments is shown in Tables XVII and XVIII, where the observed and calculated values of W are placed side by side.

10. The values of the quantities K , q , D , α_1 and α_2 which were used in these calculations, and which were found to give the best agreement between experiment and theory, are as follows:

Dissociation Constant K.—Let us define the dissociation constant K by the equation:

$$(22) \quad K = p_1^2/p_2$$

p_1 and p_2 being the partial pressures (in mm.) of atomic and molecular hydrogen, respectively. Then it is found that

$$(65) \quad \log_{10} K = 7.77 - 19700/T.$$

Values of K calculated from this equation for temperatures from 1200 to 4000° have been given in Table XV, together with the corresponding degrees of dissociation at pressures of 760 mm. and 1 mm. The following is a comparison of these results with those obtained previously (in the year 1912):

DEGREE OF DISSOCIATION AT 760 MM.

| | | | | | |
|----------------------|--------|-------|-------|------|------|
| Temp. ° K..... | 2000 | 2300 | 2500 | 3100 | 3500 |
| Results in 1912..... | 0.0013 | 0.012 | 0.039 | 0.44 | 0.84 |
| Results in 1915..... | 0.0033 | 0.014 | 0.031 | 0.17 | 0.34 |

In the range from 2200–2600°, the results are nearly identical, but at higher and lower temperatures the differences become large.

Heat of Formation of Hydrogen Molecules.—By applying van't Hoff's equation to the foregoing data, we find the heat of reaction for two grams of hydrogen to be

84000 calories at constant volume
90000 calories at constant pressure

In 1912 the value given was 130000 calories at constant volume.

Diffusion Coefficient of Atomic Hydrogen in Molecular Hydrogen.—This quantity is found to be

$$(70) \quad D = 2.14 \cdot 10^{-3} T^{3/2}.$$

This result is 4.2 times greater than that found previously by calculation from the principles of the kinetic theory. This difference suggests that the hydrogen molecules are more or less "transparent" to hydrogen atoms. The effect is probably quite analogous to that of the abnormal mobility of the H and OH ions in aqueous solutions.

The Coefficients α_1 and α_2 .—The coefficient α_1 is found to be constant and equal to unity, while α_2 is apparently constant and equal to 0.68. In other words, *all the hydrogen atoms striking the filament are absorbed by it and 68% of all the hydrogen molecules are absorbed.* The velocity of the reaction is thus determined practically entirely by the equilibrium conditions within the wire. The fact that these coefficients are found to be so nearly equal to unity is excellent evidence that in the present theory we are actually dealing with the fundamental factors determining the velocity of the reaction.

II. Other possible theories of the mechanism of the reaction are discussed, but no other is found which agrees at all well with the facts.

12. The apparent increase in specific heat caused by the dissociation is calculated. Even at temperatures as low as 2000° the effect should be perceptible. The magnitude of the effects found is, according to statements of Seigel, of the right order to account fully for certain anomalies in the experiments of Bjerrum. Therefore, the results of the explosion method, instead of conflicting with the present determinations of the degree of dissociation, may be regarded as additional evidence in their favor.

13. The rate at which hydrogen at very low pressures is dissociated by a tungsten wire at $1200\text{--}1500^{\circ}$ has been calculated according to the theory and is found to be 8–10 times greater than the *greatest* observed rate at which active hydrogen was deposited on glass surfaces. In view of the marked fatigue effects characteristic of this adsorption of active hydrogen by glass, the agreement is close enough to lend further support to the theory. The quantitative evidence of the dissociation of hydrogen may therefore be said to extend over a temperature range from 1200 to 3500°K. , in which the degree of dissociation increases in the ratio 1:170000.

14. Experiments on the heat losses from tungsten wires in mixtures of nitrogen and hydrogen yield results also in accord with the theory. See Table XXI. The diffusion coefficient of hydrogen atoms through nitrogen is found to be

$$D = 2.5 (T/273)^{3/2}$$

which is in excellent agreement with a value calculated by the kinetic theory.

SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE FREE ENERGY OF SOME CARBON COMPOUNDS.

By GILBERT N. LEWIS AND MERLE RANDALL.

Received December 15, 1914.

Elementary Forms of Carbon.

Of the numerous known forms of carbon only two, graphite and diamond, appear to be true chemical individuals. Indeed it is possible that substances like coal, charcoal, and coke should be regarded, not as elementary carbon, but as mixtures of hydrocarbons of low hydrogen content. Passing from benzene through naphthalene to more unsaturated compounds of higher molecular weight there seems to be no limit to the ratio between the number of carbon atoms to the number of hydrogen atoms in a hydrocarbon molecule. However, there are certain of the so-called amorphous forms of carbon, such as the one produced by the decomposition of pure carbon monoxide, which must be regarded as pure, but of which the properties vary according to the method of preparation. They

may consist of very minute crystals of varying size, but it is more probable that they should be regarded as liquids of enormous viscosity, or even sponge-like gels, of which the density, heat capacity and other characteristic properties are determined by the conditions under which they are formed.

In determining the difference in free energy of the elementary forms of carbon, it is impossible to proceed as we have in the case of sulfur, since no transition points are known. Schenck and Heller¹ believed that they had discovered, in the equilibrium between carbon, iron, ferrous oxide, and the oxides of carbon, different equilibrium pressure curves for the different modifications of carbon, the pressure being higher with amorphous carbon and diamond than with graphite. Theoretically it is barely conceivable that, by the intervention of a phenomenon analogous to supercooling, true equilibria involving in one case diamond and in another case graphite might be obtained. But it has been shown by Falcke² that under the conditions of Schenck and Heller's experiments this certainly is not the case. Pring and Fairlie³ in their investigation of the equilibrium between carbon, hydrogen, and methane obtained in all cases a larger proportion of methane with amorphous carbon than with graphite, but on standing, with amorphous carbon, the percentage of methane diminished as the carbon became graphitized, until the conditions obtained with pure graphite were established. It is possible that in the early stages of their experiments with amorphous carbon there was a close approach to equilibrium between this substance and the gaseous mixture. Aside from these investigations we have no chemical data which enable us to calculate the difference in free energy of the forms of carbon.

In order, therefore, to determine the difference in free energy between the two modifications of definite properties, graphite and diamond, we shall make use of a method which we have not hitherto employed in these calculations. Numerous attempts have been made to calculate free energy changes from thermal data alone, notably by Nernst and his collaborators. For the most part these calculations have involved assumptions of only approximate validity, such as Trouton's rule or the Nernst theorem concerning the so-called chemical constants. But one generalization has been developed which appears to possess universal validity. It was first clearly stated by Planck, and may be called the Second Law of Entropy. We may express this law as follows: *Every substance⁴ possesses zero entropy at the absolute zero of temperature.*

¹ Schenck and Heller, *Ber.*, 38, 2139 (1905).

² Falcke, *Ber.*, 46, 743 (1913).

³ Pring and Fairlie, *J. Chem. Soc.*, 101, 91 (1912).

⁴ This law is true of every actual substance. The entropy of an ideal gas, that is, of a gas at zero pressure, is indeterminate at the absolute zero.

Let us consider one mol. of a substance, of which the heat capacity at constant pressure is C_p . Now if it be cooled at constant pressure from the temperature T to the absolute zero, the total diminution in entropy is

$S_T - S_0 = \int_0^T \frac{C_p}{T} dT$. According to the law just stated $S_0 = 0$. Hence

$$S_T = \int_0^T \frac{C_p}{T} dT = \int C_p d \ln T. \quad (1)$$

Now in any chemical reaction $aA + bB + \dots = cC + dD + \dots$, if S_A is the molal entropy of A , etc.,

$$\Delta S = cS_C + dS_D + \dots - aS_A - bS_B - \dots$$

If the heat capacity of each substance, at the pressure at which it occurs in the reaction, is known as a function of the temperature, down to the absolute zero, we may calculate the entropy of each substance at the temperature in question and thus obtain ΔS for the reaction. But we also have the thermodynamic relation,

$$T\Delta S = \Delta H - \Delta F; \quad (2)$$

hence if the heat of reaction and the heat capacity curves of the several substances are accurately known we may determine exactly the value of ΔF .

The calculation of the entropy from the heat capacity curves can be carried out with a high degree of accuracy in many cases, owing to the fact that, since the heat capacity falls so rapidly with diminishing temperature, the range of very low temperatures, where accurate measurements are most difficult, contributes almost nothing to the entropy. According to the theory of Debye¹ the heat capacity of crystalline substances belonging to the regular system is proportional to the cube of the temperature, and Lewis and Adams² have shown that it is probable that this is true of all substances at very low temperatures. In the range of validity of this law it follows from (1) that

$$S = 1/3 C_p. \quad (3)$$

At higher temperatures we might obtain the integral of Equation 1 by the use of one of the various heat capacity equations that have been proposed. But a far simpler method, which is perfectly general and involves no assumptions, consists in plotting C_p as ordinate and $\ln T$ as abscissa and determining the area under the curve up to the temperature in question. We shall illustrate this method in determining the difference in free energy between graphite and diamond.

$C_G = C_D$.—Since graphite is not only the stable form, but is also the

¹ Debye, *Ann. Physik.*, **39**, 789 (1912).

² Lewis and Adams, *Physic. Rev.*, [2] **4**, 331 (1914).

one which has been used in high temperature equilibrium measurements, we shall consider it the standard state of elementary carbon. The most reliable measurements of the heat capacity of diamond and of graphite seem to be those of Weber¹ at high temperatures, and of Nernst² of and Koerpf³ at low temperatures. We have attempted in Fig. 1 to give the most probable curves

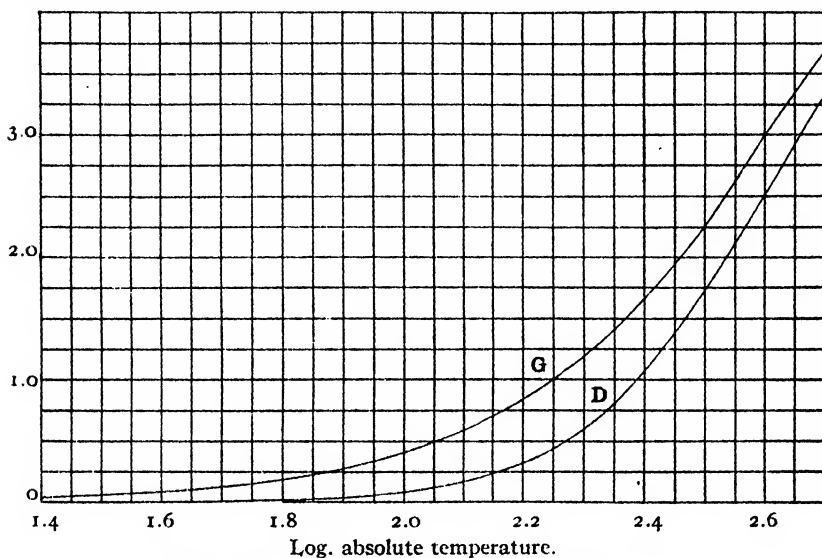


Fig. 1.—Heat Capacity of Diamond and Graphite.

on the basis of existing data for the heat capacities of the two substances.⁴ The ordinates are the values of C_p , the molal heat capacity, in calories per degree, and the abscissas are the common logarithms of T . It is evident that the area under the diamond curve below the temperature

¹ Weber, *Phil. Mag.*, [4] 49, 161, 276 (1875); *Ann. Physik. Chem.*, [2] 154, 367 (1875).

² Nernst, *Ann. Physik.*, [4] 36, 395 (1911).

³ Koerpf, *Ibid.*, [4] 36, 49 (1911).

⁴ At the highest temperatures the results of Weber were obtained by comparing diamond and graphite with platinum dropped from the same temperature into a double calorimeter. His furnace temperatures were estimated from the best data then existing for the specific heat of platinum. Those values now appear to be erroneous and we have, therefore, recalculated Weber's results at the three high temperatures where this method was employed, using White's formula for the specific heat of platinum, *Am. J. Sci.*, [4] 28, 334 (1909). We thus find for C_p (graphite) 4.85 at 950° A, 4.88 at 1150°, 4.95 at 1320°; and C_p (diamond) 4.80 at 913° A, 4.88 at 1124°, 4.82 at 1331°. It is to be noted, however, that Weber's results at lower temperatures as well as the theoretical curve obtained for diamond as a substance in the regular crystalline system, point to values nearer to those originally given by Weber, and it is possible that through some compensating error his results as originally given are more accurate than our recalculated values.

corresponding to $\log T = 1.4$ is entirely negligible. At this low temperature the graphite has not yet reached the point where it obeys the T^3 law, but we estimate that the entropy at this temperature is about 0.03, an almost negligible amount. By counting squares up to $T = 298.1$, $\log T = 2.474$, we find for the area under the graphite curve 47.80 of the squares shown in the figure. Owing to the scale of the plot, and to the fact that we are using common logarithms, we must multiply this figure by $2.303/80$ and thus obtain 1.37; adding 0.03 we find for graphite $S_{298} = 1.40$. Similarly we find for diamond $S_{298} = 0.60$. Hence we find for our reaction

$$\Delta S_{298} = -0.80 \text{ cal. per degree.} \quad (4)$$

The older determinations of the heats of combustion of graphite and diamond were too inaccurate to give ΔH , but the recent very careful work of Roth and Wallasch¹ indicates that the heat of combustion of diamond is larger than that of graphite by 280 cal. Thus $\Delta H_{298} = 280$. In general $\Delta F = \Delta H - T\Delta S$, hence

$$C_G = C_D; \Delta F^\circ_{298} = 280 + 298 \times 0.80 = 520. \quad (5)$$

Another form of our fundamental free energy equation is

$$d(\Delta F)/dT = -\Delta S.$$

If the statement of Weber is correct that at higher temperatures the heat capacity of diamond approaches but never exceeds that of graphite, then ΔS is always negative, and ΔF remains positive at all temperatures, increasing with increasing temperatures. At all temperatures, therefore, graphite is more stable than diamond at atmospheric pressure. In the formation of diamond, then, we may have another illustration of the frequent phenomenon that an unstable modification appears before the stable one has an opportunity to form. But if diamond is formed at very high pressures it may be the stable form, and if the value given above for ΔF°_{298} is correct we may calculate the transition pressure. Taking the volume per gram atom of diamond as 3.4 cc., and of graphite as 5.5 cc., the increase in free energy of either substance in compression from 1 atmos. to p atmos. is (neglecting the compressibility) $\Delta F = v(p - 1)$.² Substituting the atomic volumes and converting from cubic centimeter-atmospheres to calories, and using the above value of ΔF°_{298} we find that at room temperature diamond will be more stable than graphite at pressures above 10,000 atmos. At higher pressures, assuming any reasonable values for the coefficient of expansion, the transition pressure will increase rather than diminish.

Oxides of Carbon.

$C + CO_2 = 2CO$.—The equilibrium between carbon, carbon monoxide and carbon dioxide has been studied by several investigators. The work

¹ Roth and Wallasch, *Ber.*, 46, 896 (1913).

² Lewis, "Free Energy of Chemical Substances," Equation 11, *THIS JOURNAL*, 35, 16 (1913).

of Boudouard¹ gave the order of magnitude of the equilibrium constant and its change with the temperature, but his work has been superseded by the very careful measurements of Rhead and Wheeler.² In their experiments, wood charcoal was used, which was treated with chlorine at 1000° for 24 hrs., and later with other gases for several days at the same temperature, so that we may assume that their carbon was, at least on the surface, in the form of graphite. The heat capacity of an element at temperatures below the range of validity of the law of Dulong and Petit cannot be represented by a simple algebraic expression. We find, however, that the heat capacity curve of graphite, between 0° C. and 2000° C. may be fitted with sufficient accuracy for our purpose by the quadratic equation,

$$C_p; C_p = 1.1 + 0.0048T - 0.0000012T^2. \quad (6)$$

From our previous paper,³

$$\text{CO}_2; C_p = 7.0 + 0.0071T - 0.00000186T^2.$$

$$\text{CO}; C_p = 6.5 + 0.0010T.$$

Hence

$$\Delta F = 4.9 - 0.0099T + 0.00000306T^2.$$

$$\Delta H = \Delta H_0 + 4.9T - 0.00495T^2 + 0.00000102T^3.$$

$$\Delta F^\circ = \Delta H_0 - 4.9T \ln T + 0.00495T^2 - 0.00000051T^3 + IT.$$

The value of ΔH_{291} can be obtained from the heat of formation of CO_2 from graphite which is given by Roth and Wallasch⁴ as 94250, and from the heat of combustion of CO for which Berthelot gives 68300 and Thomsen 67960, the mean being 68100. Combining these two values $\Delta H_{291} = 41950$, and from the above equation $\Delta H_0 = 40910$.

The values of I at the various temperatures of Rhead and Wheeler's measurements can now be obtained, and are given in Table I, in which

TABLE I.

| T. | % CO. | % CO ₂ . | K. | ΔF° . | I. |
|------|-------|---------------------|-------|--------------------|--------|
| 1123 | 93.77 | 6.23 | 14.11 | -5900 | -12.16 |
| 1173 | 97.78 | 2.22 | 43.07 | -8760 | -12.73 |
| 1223 | 98.68 | 1.32 | 73.77 | -11190 | -12.43 |
| 1273 | 99.41 | 0.59 | 167.5 | -12940 | -12.72 |
| 1323 | 99.63 | 0.37 | 268.3 | -14680 | -12.46 |
| 1373 | 99.85 | 0.15 | 664.7 | -17720 | -13.15 |
| 1473 | 99.94 | 0.06 | 1665 | -21690 | -12.95 |

Average, -12.66

¹ Boudouard, *Compt. rend.*, 130, 132 (1900).

² Rhead and Wheeler, *J. Chem. Soc.*, 97, 2178 (1910). In the recent work of Clement, U. S. Bureau of Mines, *Bull.* 17 (1911), the rate of this reaction was chiefly studied. His estimate of the equilibrium constant is evidently erroneous, owing to the fact that his experiments were of too short duration to permit the attainment of equilibrium conditions.

³ Lewis and Randall, *This Journal*, 34, 1128 (1912).

⁴ Roth and Wallasch, *loc. cit.*

the first column gives the absolute temperatures, the next two the percentages of CO and of CO₂ in the equilibrium mixture at atmospheric pressure, the fourth the equilibrium constant, the fifth $\Delta F^\circ = -R'T \ln K$, and the sixth the values of I obtained from the several values of ΔF° .

The values of I show excellent constancy, and considering the difficulties of the experiment, this must be regarded as one of the most satisfactory investigations of high temperature equilibrium. Using the mean value of I we have



$$\Delta F^\circ = 40910 - 4.9T \ln T + 0.00495T^2 - 0.0000051T^3 - 12.66T. \quad (7)$$

$CO_2 + H_2 = CO + H_2O(g)$.—This reaction, known as the water gas reaction, has been the subject of numerous investigations. The formulas for the heat capacities of these four gases are given in our previous paper¹ from which we find

$$\Delta G = 1.81 - 0.0089T + 0.00000408T^2.$$

For the formation of water vapor from its elements, $\Delta H_o = -57410$,² and for the formation of carbon dioxide from carbon monoxide and oxygen, $\Delta H_o = -67510$ as we show in the next reaction. Hence for the water gas reaction $\Delta H_o = 10100$ and

$$\Delta F^\circ = 10100 - 1.81T \ln T + 0.00445T^2 - 0.00000068T^3 - 0.54T. \quad (8)$$

The value of I = -0.54 is obtained from the important determinations of the equilibrium in this reaction by Hahn³ and by Haber and Richardt.⁴ Their results are summarized in Tables II and III. The first row gives the absolute temperature of the measurements, the second the equilibrium constant, and the third the value of I calculated therefrom.

TABLE II (HAHN).

| | | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| T.... | 959 | 1059. | 1159 | 1209 | 1278 | 1359 | 1478 | 1678 |
| K.... | 0.534 | 0.840 | 1.197 | 1.571 | 1.620 | 1.960 | 2.126 | 2.490 |
| I.... | -0.59 | -0.53 | -0.56 | -0.79 | -0.49 | -0.50 | -0.23 | 0.06 |

TABLE III (HABER AND RICHARDT).

| | | | | | | | | | | |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| T..... | 1503 | 1528 | 1538 | 1582 | 1597 | 1643 | 1768 | 1783 | 1797 | 1824 |
| K..... | 3.05 | 2.68 | 2.85 | 2.72 | 2.93 | 3.26 | 3.83 | 3.66 | 3.86 | 3.56 |
| I..... | -0.65 | -0.51 | -0.58 | -0.37 | -0.47 | -0.64 | -0.61 | -0.47 | -0.55 | -0.32 |

In Hahn's work the gases were allowed to stream by a catalyzer and were rapidly cooled, but, as pointed out by Haber⁵ in his critical résumé of this equilibrium, the discrepancy between Hahn's measurements at high and low temperatures is due to the difficulty in cooling the mixture from a high temperature rapidly enough to prevent the continuance of the re-

¹ Lewis and Randall, *THIS JOURNAL*, **34**, 1128 (1912).

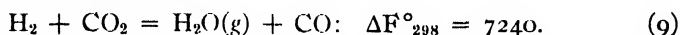
² Lewis and Randall, *Ibid.*, **36**, 1981 (1914).

³ Hahn, *Z. physik. Chem.*, **44**, 513 (1903); **48**, 735 (1904).

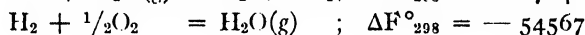
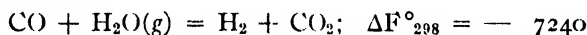
⁴ Haber and Richardt, *Z. anorg. Chem.*, **38**, 5 (1904).

⁵ Haber, "Thermodynamics of Technical Gas Reactions."

action. This criticism apparently does not hold for Hahn's lower temperatures and we may take from his first three measurements $I = -0.56$. The measurements of Haber and Richardt were obtained by a study of the temperature and composition of the gases in the free flame. The agreement of the values of I with one another, and with those of Hahn at low temperature, not only give us great confidence in the reliability of the experimental results, but also in the equations which we have chosen to express the heat capacities of the several gases involved. The discussion given in Haber's book shows how extremely difficult it is to interpret high temperature equilibrium measurements when there is any serious doubt concerning the true heat capacity values. We have chosen as a final mean $I = -0.54$, hence



$\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2$.—Another important check upon the calculation just made is furnished by the study of the dissociation of carbon dioxide, for by combining (8) with Equation 56 of our paper on oxygen and hydrogen compounds,



We may now proceed to calculate the free energy of this reaction from direct measurements of the dissociation of carbon dioxide. The heat capacity values we shall take once more from our paper on specific heats and find $\Delta I' = -2.75 + 0.0056T - 0.00000186T^2$. We have already found $\Delta H_{291} = -68100$, whence $\Delta H_0 = -67510$ and

$$\Delta F^\circ = -67510 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 + IT.$$

The calculation of I from the experiments of Nernst and von Wartenberg,¹ Langmuir² and Löwenstein³ is shown in Table IV. The first column gives the absolute temperature of the measurements, the second

TABLE IV.

| T. | % dissociation. | K. | I. | |
|------|-----------------|--------|------|---------------------------|
| 1395 | 0.0142 | 837000 | 4.67 | Langmuir |
| 1400 | 0.015 | 781000 | 4.61 | Nernst and von Wartenberg |
| 1443 | 0.025 | 358000 | 4.76 | Langmuir |
| 1478 | 0.032 | 247000 | 4.39 | Nernst and von Wartenberg |
| 1481 | 0.028 | 295000 | 3.94 | Langmuir |
| 1498 | 0.047 | 138000 | 4.89 | Langmuir |
| 1565 | 0.064 | 87300 | 4.91 | Langmuir |
| 1823 | 0.4 | 5600 | 3.28 | Löwenstein |

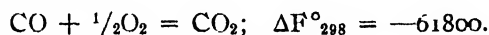
¹ Nernst and von Wartenberg, *Z. physik. Chem.*, **56**, 548 (1906).

² Langmuir, *THIS JOURNAL*, **28**, 1357 (1906).

³ Löwenstein, *Z. physik. Chem.*, **54**, 707 (1905).

the percentage dissociation of carbon dioxide at atmospheric pressure, the third the equilibrium constant $p_{\text{CO}_2}/(p_{\text{CO}}p_{\text{O}_2}^{1/2})$, the fourth the value of I, and the fifth the author.

The mean of the several values of I is 4.43, or 4.69 if we exclude the uncertain value of Löwenstein and the one exceptionally low value of Langmuir. On the other hand by direct subtraction of Equation 8 for the water gas reaction from Equation 56 of our previous paper for the free energy of formation of water vapor we find $I = 4.26$. The agreement is very satisfactory. We shall give greater weight to the water gas reaction which was studied at lower temperatures and choose $I = 4.30$ as the final value, whence



$$\Delta F^\circ = -67510 + 2.75T \ln T - 0.0028T^2 + 0.00000031T^3 + 4.30T. \quad (10)$$

$\text{C}_\text{G} + \frac{1}{2}\text{O}_2 = \text{CO}$.—Adding Equations 7 and 10 gives

$$\Delta F^\circ = -26600 - 2.15T \ln T + 0.00215T^2 - 0.0000002T^3 - 8.36T. \quad (11)$$

$$\Delta F^\circ_{298} = -32560.$$

$\text{C}_\text{G} + \text{O}_2 = \text{CO}_2$.—Adding Equations 10 and 11,

$$\Delta F^\circ = -94110 + 0.60T \ln T - 0.00065T^2 + 0.00000011T^3 - 4.06T. \quad (12)$$

$$\Delta F^\circ_{298} = -94360.$$

Carbonic Acid and Its Ions.

$\text{CO}_2 + \text{H}_2\text{O}(\text{l}) = \text{H}_2\text{CO}_3(\text{aq})$.¹—The solubility of CO_2 in water at 25° at a partial pressure of $\frac{1}{4}$ atmos. is 0.0338 mols per liter according to the entirely concordant measurements of Bohr and Bock² and of Just.³ Hence

$$\Delta F^\circ_{298} = -R'T \ln 0.0338 = 2010. \quad (13)$$

$\text{H}_2 + \text{C}_\text{G} + \frac{3}{2}\text{O}_2 = \text{H}_2\text{CO}_3(\text{aq})$.—Adding Equations 12, 13, and Equation 54 of our previous paper,

$$\begin{array}{ll} \text{C}_\text{G} + \text{O}_2 = \text{CO}_2 & ; \Delta F^\circ_{298} = -94360 \\ \text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3(\text{aq.}) & ; \Delta F^\circ_{298} = 2010 \\ \text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}(\text{l}) & ; \Delta F^\circ_{298} = -56620 \end{array}$$

$$\text{H}_2 + \text{C}_\text{G} + \frac{3}{2}\text{O}_2 = \text{H}_2\text{CO}_3(\text{aq.}); \Delta F^\circ_{298} = -148970 \quad (14)$$

$\text{H}_2\text{CO}_3(\text{aq.}) = \text{H}^+ + \text{HCO}_3^-$.—Walker and Cormack⁴ found for the first dissociation constant of carbonic acid $K_{291} = 3.04 \times 10^{-7}$. The heat of this reaction is the heat of mixture of 1 mol H_2CO_3 and 1 mol NaOH , less the heat of neutralization of 1 equivalent of a strong acid. From

¹ Of course we make no assumption that the carbon dioxide dissolved in water is all in the form of H_2CO_3 . For the purpose of the thermodynamic calculations in which we are engaged it is immaterial whether the substance is all H_2CO_3 , or in part CO_2 or higher hydrates than H_2CO_3 .

² Bohr and Bock, *Ann. Physik*, [3] 44, 318 (1891).

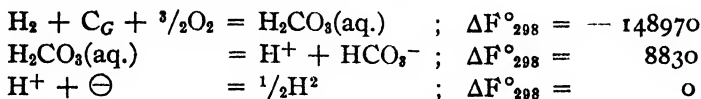
³ Just, *Z. physik. Chem.*, 37, 342 (1901).

⁴ Walker and Cormack, *J. Chem. Soc.*, 77, 5 (1900).

Thomsen's measurements $\Delta H = 2700$, and, applying the van't Hoff formula, $K_{298} = 3.39 \times 10^{-7}$. Hence

$$\Delta F_{298}^{\circ} = 8830. \quad (15)$$

$\frac{1}{2}\text{H}_2 + \text{C}_G + \frac{3}{2}\text{O}_2 + \ominus = \text{HCO}_3^-$.—Combining Equations 14, 15, and Equation 9 of our previous paper,



$$\frac{1}{2}\text{H}_2 + \text{C}_G + \frac{3}{2}\text{O}_2 + \ominus = \text{HCO}_3^-; \Delta F_{298}^{\circ} = -140140 \quad (16)$$

$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{--}$.—The second dissociation constant of carbonic acid has been the subject of investigations by Bodländer,¹ McCoy,² and Auerbach and Pick.³ The uncertainty in this constant seems to be due not so much to the experiments as to the difficulty of interpreting them. We know very little about the concentration of the ion NaCO_3^- or about the concentration and activity of CO_3^{--} in mixtures of sodium carbonate

and acid carbonate. McCoy determined the ratio $\frac{(\Sigma \text{NaHCO}_3)^2}{(\Sigma \text{H}_2\text{CO}_3)(\Sigma \text{Na}_2\text{CO}_3)}$ in solutions M , $0.3M$, and $0.1M$ with respect to NaHCO_3 , and found 3120, 4460, and 5290, respectively. By a rough extrapolation from these figures we find 6300 at high dilution, where the two salts may be regarded as completely dissociated, and the quotient becomes $\frac{(\text{HCO}_3^-)^2}{(\text{H}_2\text{CO}_3)(\text{CO}_3^{--})}$.

Dividing by this quotient the first dissociation constant of carbonic acid given above we find $K_{298} = (\text{H}^+)(\text{CO}_3^{--})/(\text{HCO}_3^-) = 5.4 \times 10^{-11}$ as the second dissociation constant of carbonic acid, whence

$$\Delta F_{298}^{\circ} = 14010. \quad (17)$$

$\text{C}_G + \frac{3}{2}\text{O}_2 + 2 \ominus = \text{CO}_3^{--}$.—Using once more the fact that the free energy of hydrogen ion is taken as zero, and combining Equations 16 and 17,

$$\Delta F_{298}^{\circ} = -126130. \quad (18)$$

Methane.

$\text{C}_G + 2\text{H}_2 = \text{CH}_4$.—Of all the hydrocarbons the only one for which we have data reliable enough to warrant the present calculation of the free energy is methane.

The specific heat of methane has been determined only through a small range of temperatures. Regnault found $C_p = 9.5$ at about 108° . As might be expected, this is a somewhat higher value than that given by the

¹ Bodländer, *Z. physik. Chem.*, **35**, 23 (1900).

² McCoy, *Am. Chem. J.*, **29**, 437 (1903).

³ Auerbach and Pick, *Arb. Kais. Gesundheits.*, **38**, 243 (1911).

equation for ammonia. We will modify (1) and write

$$CH_4: C_p = 7.5 + \quad (19)$$

Combining this with the equation already given for hydrogen and graphite,

hydrogen and graphite,

$$\Delta F = -6.6 - 0.0016T + 0.0000012T^2.$$

The heat of combustion of methane to form gaseous CO_2 and liquid H_2O is 212400 according to Thomsen, and 212800 according to Berthelot, mean 212600. The heat of formation of liquid water we have shown in a previous paper to be 68470 at $0^\circ C.$, or 68330 at 18° . Using the heat of combustion of graphite, which we have already taken from the work of Pring and Wallasch, we find for the formation of methane from its elements $\Delta H_{291} = -18300$, and from the equation for ΔF , $\Delta H_0 = -16300$, and $\Delta F^\circ = -16300 + 6.6T \ln T + 0.0008T^2 - 0.0000002T^3 + IT$.

Measurements of equilibrium in the reaction were made by Mayer and Altmayer.

more extensive measurements.

These authors obtained a higher yield of methane from amorphous carbon than from graphite, but in the latter case a true equilibrium was reached, whereas in the former the equilibrium continually changed owing to the gradual transition from amorphous carbon to graphite. The ultimate equilibrium was the same as that obtained directly from graphite. We shall give in Table V the various results obtained by Pring and Fairlie without distinguishing between the different varieties of graphite which they used. The first column shows the absolute temperature, the second the equilibrium constant $p_{CH_4}/p_{H_2}^2$, and the third the corresponding value of I . The first value given represents the average of the measurements of Mayer and Altmayer at $823^\circ A$ with amorphous charcoal, which was covered with a catalyzer of nickel or cobalt and was presumably graphitized in part.

TABLE V.

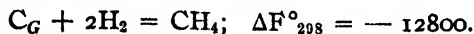
| T. | K. | I. | T. | K. | I. |
|-------|---------|---------|------|---------|-------|
| (823) | (0.64) | (-24.2) | 1673 | 0.00103 | -26.4 |
| 1473 | 0.00244 | -25.9 | 1673 | 0.00089 | -26.1 |
| 1548 | 0.00147 | -25.8 | 1673 | 0.00089 | -26.1 |
| 1573 | 0.00146 | -26.0 | 1723 | 0.00075 | -26.1 |
| 1573 | 0.00158 | -26.2 | 1773 | 0.00077 | -26.7 |
| 1648. | 0.00100 | -26.1 | 1848 | 0.00062 | -27.0 |
| 1648 | 0.00117 | -26.4 | | | |

There is evidently a slight trend of I with the temperature. This may be

¹ Mayer and Altmayer, *Ber.*, **40**, 2134 (1907).

² Pring and Fairlie, *J. Chem. Soc.*, **101**, 91 (1912). In this paper and in previous papers by the same authors the equilibrium conditions are investigated in the formation, not only of methane, but of ethylene and acetylene. However, we have regarded the experimental data, in the case of the latter hydrocarbons, as too uncertain to make complete free energy calculations desirable at present.

due to an error in the equation assumed for the heat capacity of methane but it may also be an experimental error, the possibility of which the authors themselves have pointed out, namely, an excessive yield of methane at high temperatures owing to the indirect formation of methane, during the rapid cooling of the gas for analysis, from other hydrocarbons which may be present at high temperatures. In either case it would be advisable to give a little more weight to the values at low temperatures and we may take $I = 26.0$. Hence



$$\Delta F = -16300 + 6.6T \ln T + 0.0008T^2 - 0.0000002T^3 - 26.0T. \quad (20)$$

Carbon Oxychloride.

$CO + Cl_2 = COCl_2(g)$.—In the absence of any reliable measurements of the heat capacity of phosgene we may assume it to be the same as that of ammonia. With the aid of the equations of CO and Cl_2 previously used $\Delta F = -5.5 - 0.0008T$. Between the values of the heat of this reaction obtained by Thomsen and Berthelot there is a great discrepancy. Thomsen obtains 27000 cal. and Berthelot 19000, which give, respectively, $\Delta H_o = -25000$; $\Delta H_o = -17000$. The value of Berthelot seems to be the more reliable and is in agreement with one calculated from the equilibrium measurements of Bodenstein and Dunant¹ which we are about to discuss. We shall take $\Delta H_o = -18000$, and

$$\Delta F^\circ = -18000 + 5.5T \ln T + 0.0004T^2 - 14.1T. \quad (21)$$

The value of I is obtained from determinations by Bodenstein and Dunant of the dissociation of $COCl_2$ at the three temperatures given in Table VI. From the value of I , $\Delta F^\circ_{298} = -12820$.

TABLE VI.

| T. | % dissociation. | K. | I. |
|-----|-----------------|-------|-------|
| 776 | 67 | 1.227 | -14.1 |
| 826 | 80 | 0.560 | -14.3 |
| 876 | 91 | 0.208 | -14.0 |

$C_G + \frac{1}{2}O_2 + Cl_2 = COCl_2(g)$.—Combining Equations 11 and 21 gives $\Delta F^\circ_{298} = -45380$, and

$$\Delta F = -44600 + 3.35T \ln T + 0.00255T^2 - 0.0000002T^3 - 22.46T. \quad (22)$$

We wish to express our obligation to the Rumford Fund of the American Academy of Arts and Sciences for financial aid in this investigation.

Summary.

The following table gives the free energy of formation of the various compounds of carbon considered in this paper.

¹ Bodenstein and Dunant, *Z. physik. Chem.*, 61, 437 (1907).

TABLE VII.

| Substance. | F° _m . | Equation. | Substance. | F° _m . | Equation. |
|--------------------------------------|-------------------|-----------|-------------------------------|-------------------|-----------|
| Diamond | 520 | 5 | HCO ₃ ⁻ | -140140 | 16 |
| CO(g) | -32560 | 11 | CO ₃ ⁻ | -126130 | 18 |
| CO ₂ (g) | -94360 | 12 | CH ₄ | -12800 | 20 |
| H ₂ CO ₃ (aq.) | -148970 | 14 | COC1 ₂ | -45380 | 22 |

BERKELEY, CAL.

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

COMPRESSIBILITIES OF MERCURY, COPPER, LEAD, MOLYBDENUM, TANTALUM, TUNGSTEN AND SILVER BROMIDE.

BY THEODORE W. RICHARDS AND EDWARD P. BARTLETT.

Received January 6, 1915.

The compressibilities of the elements are data of great interest, in common with all the other properties of these fundamental substances. Until recently, however, they received but little attention. Six years ago, for the first time, results for a large number of elements, consistently determined by a new and adequate method, were available.¹ From these results it became clear that compressibilities, like many other properties of the elements, are highly periodic in their nature as referred to the progressively increasing atomic weights. Since that time much interest has been taken in the subject, and Bridgman,² at the Jefferson Physical Laboratory at Harvard University, and Grüneisen,³ at the Physikalisch-technische Reichsanstalt in Berlin, have both thrown further light upon it. In the main, these results have confirmed and amplified the earlier Harvard results, but there remain two or three points of difference to be explained, and, moreover, it seemed highly desirable to extend the list of elements. Hence the present investigation was undertaken with both of these aims in view. The method employed was precisely that used in preceding investigations,⁴ except that in our most accurate work the piezometer was made of soft steel instead of glass. For the details the reader is referred to earlier publications.

In brief, the method consisted in the determination of the difference between the compressibility of each substance in question and that of mercury, which was itself determined by reference to iron. The linear compressibility of iron has been absolutely determined by Bridgman. The piezometer used in the present investigation consisted of a cylindrical vessel of glass or soft steel filled with mercury, being so arranged that the

¹ Richards, Stull, Brink and Bonnet, *Pub. Carnegie Inst. Wash.*, No. 76 (1907); *Z. physik. Chem.*, 61, 77, 183 (1908); *THIS JOURNAL*, 31, 154 (1909).

² Bridgman, *Proc. Amer. Acad.*, 47, 347 (1911).

³ *Ann. phys.*, 25, 825 (1908); 33, 1239 (1910).

⁴ See for example *THIS JOURNAL*, 34, 971 (1912); see also Stähler's "Handbuch der Arbeitsmethoden in der anorganischen Chemie," Vol. III, p. 246 (1912).

only free surface of this liquid metal was exposed in a capillary tube, which made it possible to measure very small changes of volume. The level of the mercury in this capillary tube was determined by a very finely pointed platinum wire, which completed an electrical circuit. Successive weighed drops of mercury were added in this tube, and the relation between the weight of this added mercury and the pressure necessary to compress the system exactly to the attainment of electrical contact was determined in each case. In this way, at first mercury alone was compressed in the piezometer, and the relation of the added mercury to the increasing pressure was found. Subsequently, each other substance in turn was completely immersed in the mercury, and the operation repeated. Obviously, if the immersed substance had the same compressibility of mercury, a curve precisely similar to the first would have been attained, but, as all the substances discussed in this paper had a less compressibility than mercury, the curves were different from that obtained when mercury alone was present, in such a sense that for a given weight of added mercury a greater pressure was necessary than with mercury alone in the piezometer. Diagrams of the two forms of piezometer will help to make the matter clear.

The glass piezometer (Fig. 1) has been described in detail before.¹ Although the steel piezometer was somewhat different in arrangement, the principle is exactly the same. It consisted of a hollow steel cylinder, K, closed at the bottom, which had been turned and bored from a heavy rod of steel. (Figs. 2 and 3.) Upon the top of this was clamped, by a powerful screw, a cover, G, containing the capillary. Below this cover was secured a little pail or capsule, J, to hold mercury, in case a lighter liquid was to be confined in the piezometer itself. This pail or capillary would, of course, be unnecessary if no liquid besides mercury were present. The contact was made by a stout, steel needle, E, with a very finely pointed platinum tip, F; it was secured above in such a way as to be rigid and unchangeable in position, centered below by a light movable bracing of wires, and was insulated from the rest of the apparatus by a thin film of mica, C. This upper portion of the piezometer is shown on a large scale in Fig. 2, since the details are important, and were the outcome of much thought and experiment.

The washer, I, sealing the joint between the cylinder and its cover gave much trouble. After various attempts with lacquered lead, copper and organic substances, we finally chose soft iron, and found that, if both surfaces of the ring of soft iron were made somewhat pointed (that is to say, the cross section of the ring made of a very elongated "diamond"-shape), good contact and complete closure were effected. The volume of liquid retained by this device outside of the washer, and not under

¹ THIS JOURNAL, 34, 975 (1912).

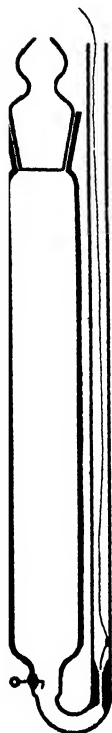


Fig. 1.

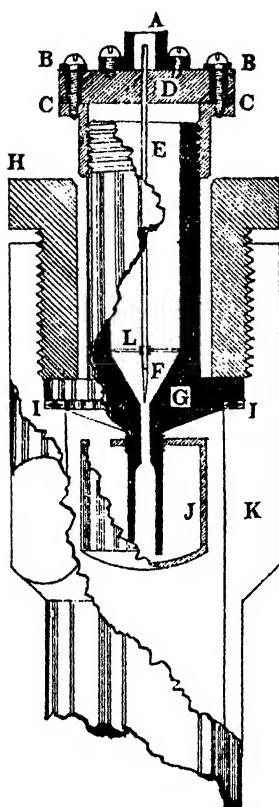


Fig. 2.

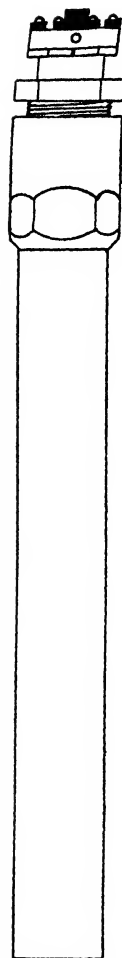


Fig. 3.

Fig. 1.—Glass piezometer.

Fig. 2.—Details of top of steel piezometer.

A, hard rubber cup to hold mercury for making contact.

B, hard rubber bushing to insulate screws.

C, joint with thin plate of insulating mica.

D, set screw to hold needle in position.

E, steel needle.

F, platinum point attached to needle.

G, steel top of piezometer held in place by

H, screw cap, and made mercury-tight by

I, soft iron washer.

J, cup to hold mercury.

K, section of cylinder-wall.

L, guide to hold needle in center.

The whole is of soft Bessemer steel, except the three rubber pieces, A, B, B, the mica plate C, and the platinum point F.

Fig. 3.—Sketch of exterior of steel piezometer when assembled.

quantitative compression was computed, and due allowance was made for it.

The pressure gauge was an absolute one, consisting of a perfectly cylindrical piston or plunger exactly fitting into an equally cylindrical hole just 0.0002 cm. larger in diameter, which communicated with the pressure pump. The apparatus had been made especially with unusual care by the Taft-Pierce Co., of Woonsocket, and had been very carefully studied and verified in all its details in an earlier research carried out by one of us in common with Dr. J. W. Shipley, as yet unpublished. Careful measurement of the piston gave us its area, to which was added half the area of the very thin ring of lubricant around it, and it was weighted with standardized weights by means of an oscillating carriage. For approximate preliminary observation of the pressure, a Bourdon gauge also was attached to the system. The pressure was applied by a Cailletet pump of the usual type, capable of giving 1000 atmospheres, and was transmitted to both of the gauges and the piezometers by castor oil, according to the recommendation of the Earl of Berkeley. The unit of pressure adopted is the megabar (or megabarie), which has been suggested on various sides and has now received international sanction.¹ It is the pressure of a megadyne per square centimeter, and is 1.3% less than an "atmosphere" or 2.0% more than 1 kg./cm². The mercury contact was indicated by a delicate galvanometer.

The substances studied were copper, iron, lead, mercury, molybdenum, tantalum, tungsten and silver bromide. The bar of copper was of pure commercial electrolytic material, and had been thoroughly hammered and turned. The iron had been several times hammered, in order that the pores which sometimes exist in iron should have been closed, and likewise annealed and turned to regular shape. It had been smelted by the American Rolling Mill Co., and contained 0.05% of impurity. The molybdenum, tantalum and tungsten were also each in a very compact condition. They were loaned through the kindness of Dr. W. R. Whitney of the General Electric Company, and were doubtless of high degree of purity. The silver bromide had been prepared in this laboratory, and was the same as that used five years ago by one of us with the collaboration of Grinnell Jones.² The mercury was carefully purified by orthodox methods.

The chief measurements were made as nearly as possible over the range from 100 to 500 megabars, the weight of added mercury, w , and the pressure, p , being carefully observed. These data were corrected, as indicated below, precisely to the pressure range just mentioned. In each case the

¹ *Rapport Internat. Cong. Phys.*, Paris, 1, 100 (1900); see also Richards and Stull, *Loc. cit.*, 1903; Guillaume, "Les récents progrès des Syst. Métrique," Paris, 1907.

² Richards and Jones, *THIS JOURNAL*, 31, 158 (1909).

half-way point, at 300 megabars, was taken also, but since these values are only of subordinate interest, they are merely averaged and summarized in the tables below, at the end of each series. They not only verified our work over the larger range, but also served the useful purpose of determining approximately the changing pitch of the curve, dw/dp , over the whole length—an outcome which made it possible to correct each initial reading exactly to 100 megabars, and each final reading exactly to 500 megabars. Evidently the average pitch, dw/dp , over the whole range is (except with very compressible substances) about that of the tangent to the curve in the middle (at 300 megabars). The average pitch over the first half corresponds closely to that of the tangent at 200 megabars, and that over the second half corresponds closely to that of the tangent at 400 megabars. The pitch at either the beginning or the end of the curve, therefore, is found by respectively adding to or subtracting from the mean value of dw/dp over the whole range, the difference between the pitches of the first and second halves of the curve, because this difference corresponds to the change in dw/dp caused by a change of pressure of 200 megabars. This method is not very exact, because its basic assumption that dw/dp varies linearly with the pressure is not quite true; but it is near enough to correct small divergences at either end of the scale as accurately as the experimental results warrant. In the case of compressible substances like water, the pitch of the curve at each end must be experimentally determined; such determinations are recorded in some cases below. The temperature was always exactly 20.00° ($\pm 0.002^\circ$) maintained by a very accurate thermostat.

The results were all calculated for exactly the range 100–500 megabars, according to the following equation:

$$\beta = \frac{(w - w' - mK)D}{5429.0 W} + \beta',$$

in which w is the weight of mercury added in the special case, and w' that added when mercury alone is present; m the additional weight of mercury needed for the range 100–500 megabars when one gram of another liquid is substituted for an equal volume of mercury, and K the weight of the other liquid; W the weight of substance and D its density; β and β' represent the compressibility sought and that of mercury, respectively.

The first step toward this, as well as towards any other work with such a piezometer, is the compression of the instrument filled with pure mercury, of which it contained 767.0 g., under atmospheric pressure. The following table recounts a series of such compressions—it shows that under 500 megabars pressure it contains about 768.3 g., the gain for 400 megabars being recorded accurately in the table below:

TABLE I.—THE COMPRESSION OF MERCURY IN STEEL.

| Range. Megabars. | Hg added. | Hg cor. 100-500 megabars. | Other data necessary. |
|---------------------|-----------|------------------------------|--------------------------|
| 97.5 — 500.3 | 1.0477 | 1.0384 | W = 767.0 |
| 109.0 — 503.9 | 1.0247 | 1.0382 | |
| 109.0 — 499.1 | 1.0123 | 1.0383 | D = 13.546 |
| 108.9 — 500.2 | 1.0158 | 1.0388 | |
| 100.0 — 300.0 | (0.5227) | | |

$$W = 1.0384$$

This table shows, in the third column, the remarkable consistency of the method under favorable conditions. It shows also that a range of 400 megabars corresponds to the added weight of 1.0384 g. of mercury when the piezometer contained 767.0 g.—a compression of about 0.135%. Substituting in the above formula (where for this special case w' , m , and K are zero) we find that $\beta' = \beta + 3.378 \times 10^{-6}$. This represents the difference between the compressibility of mercury and the soft steel of the piezometer. It is subject to two slight possibilities of error, as follows: first, the possible existence of minute holes or cracks in the steel, into which high pressure might force mercury; and, secondly, the possible slight change of form of the meniscus under pressure. If with Bridgman¹ we assume the compressibility of this steel to be 0.588×10^{-6} at 20°, the compressibility of mercury is shown by our experiments to be 3.966×10^{-6} over the range 100-500 megabars in question—a value which is probably the maximum.

Another method of using the piezometer fortunately gives us the means of entirely avoiding the second of the above-mentioned difficulties, and causes the first to affect the result in an opposite sense. This method is to immerse a somewhat rounded bar of pure iron into the piezometer, making a new series of determinations of the relation of increasing mercury to increasing pressure and calculating the results from the difference between the outcome of the two series of experiments. According to this procedure all defects in the piezometer are eliminated, occurring in both series. Results of a second series of experiments thus planned are given in Table II; a bar of soft, pure iron already described, was placed in the piezometer, displacing 20.015 cc. of the mercury; and the same determinations were made again. The preliminary trials, which served to acquaint the experimenters with the method and to determine the amount of mercury to be added in each case, are omitted, as in the table above. With exceptions of this sort, all the results in all the following tables were consecutive.

It appears from the first table that the amount of mercury added between 100 and 500 megabars, when mercury alone was present, was 1.0384, but from the second table that this amount was only 0.6758 when the

¹ Bridgman, *Proc. Am. Acad.*, 47, 366, 367 (1911).

TABLE II.—PURE IRON UNDER MERCURY IN STEEL.

| Pressure range. Megabars. | Wt. mercury added. | Wt. mercury cor. to 100-500 megabars. | Other data necessary. | $(\beta - \beta) \times 10^4$. |
|------------------------------|-----------------------|--|--------------------------|---------------------------------|
| 146.4 — 503.6 | 0.6000 | 0.6736 | $m = 0$ | —334 |
| 182.2 — 500.0 | 0.5357 | 0.6768 | $w = 1.0384$ | |
| 98.5 — 499.2 | 0.6782 | 0.6770 | $W = 157.095$ | |
| 62.4 — 503.2 | 0.7430 | 0.6734 | $D = 7.849$ | |
| 503.6 — 206.6 | 0.5014 | 0.6773 | | |
| 499.2 — 143.9 | 0.5997 | 0.6764 | | |
| 100.0 — 300.0 | (0.3399) | | | |
| Average, $= w = 0.6758$ | | | | |

bar of iron was immersed in the mercury—the difference between being 0.3626. This weight of added mercury occupied a volume of 0.02667 cc. at the highest pressure concerned, a volume which corresponds to the difference between the compression of 20.015 cc. of iron and exactly the same bulk of mercury, due to the addition of 400 megabars pressure. From this it is easy to calculate that the compressibility of mercury over this range must be 0.00000334 plus that of the pure iron.

Now Bridgman has determined, with great care, the compressibility of soft steel ("Bessemer screw-stock") under high pressures, and found that this compressibility is not appreciably affected by increasing pressure up to 10,000 atmospheres, as, indeed, one would expect because of the great internal pressure of the substance. His values in terms of the kg./cm². standard were 0.000000583 at 10° and 0.000000601 at 50°,¹ or 0.000000588 at 20°. In a recent investigation of Grüneisen, two different specimens of iron (having the densities 7.83 and 7.82, respectively) gave values between 0.000000585 and 0.000000633, determined by an indirect method depending upon the theory of elasticity.² In view of these facts, it seems to be fairly safe to assume (especially because the compressibility even of soft steel is probably slightly less than that of iron) that the compressibility of this latter metal at 20° is very near 0.00000060, if the pressure is registered in kilograms per square centimeter.³ Calculated in terms of the megabar standard, this becomes 0.00000061; and if this value is added to the difference between the compressibilities of mercury and iron (namely, 0.00000334), we find that the average compressibility of mercury over the range between 100 and 500 megabars

¹ Bridgman, *Proc. Amer. Acad.*, **47**, 366, 367 (1911).

² Grüneisen, *Ann. phys.*, **33**, 1257 (1910).

³ The early determinations of this value published by one of us in conjunction with F. N. Brink (*Pub. Carnegie Inst. Wash.*, **76**, 45 (1907)) made no pretensions to great accuracy. On page 52, in conclusion, the following statement is made: "Hence these results are to be considered merely as preliminary ones, worthy of publication because they exemplify the working of an efficient arrangement of apparatus, as well as because they confirm essentially the work of others on this subject." They yielded a result for iron distinctly lower than the results of Bridgman and Grüneisen. For suggestions as to the cause of the error, see pages 48-49 of the original paper; also Bridgman, *Ibid.*, p. 368.

is 0.00000395. This may be looked upon as the minimum value; and the average 0.00000396 of this and the maximum value (0.000003966) previously mentioned may be taken, with very slight probability of error, as the true compressibility of mercury. On the kg./cm². basis, this becomes 0.00000388, and on the "atmosphere" basis, 0.00000401. This is especially interesting and important because no other determination of modern accuracy over this pressure range seems to have been made. Bridgman's results at high pressure are admirable; but his method is not satisfactory at low pressure, and his results below 1000 atmospheres were merely extrapolated. It is interesting to note, nevertheless, that our result is in fairly close agreement with the results of Bridgman for mercury as extrapolated to our pressures. At 22° Bridgman found the change in volume between one and two thousand metric atmospheres to be 0.00377; for the third thousand, 0.00364; for the fourth thousand, 0.00353; for the fifth thousand, 0.00337; for the sixth thousand, 0.00324, as the mean of two series of determinations. Bridgman carried the work to higher pressures, but these do not concern us. The decrease in the compressibility for a thousand metric atmospheres is seen to be on the average nearly 0.00000013. Extrapolating to 300 atmospheres, the value becomes 0.00000391 per metric atmosphere, and correcting this to 20° (from Bridgman's figures at 0°) and then to the megabar standard, we obtain the value 0.00000398 for the compressibility of mercury, which is perhaps as near as could be expected (considering the extrapolation) to our value 0.00000396. Therefore, this latter value will be assumed in the rest of the present paper as the true average value over the range from 100–500 megabars.

Before proceeding to the determinations of the compressibilities of the several metals, a table should be given recording the constant for the glass piezometer, which was used in some cases. The glass piezometer, while it gives accurate results if quickly compressed and always read after exactly the same length of time (as soon as the heat of compression has been dissipated) shows marked hysteresis when the pressure is long continued. The determinations given below are all made under the same conditions, and the hysteresis-effects will be discussed in another connection later. The glass apparatus contained 385.28 g. of mercury.

TABLE III.—MERCURY IN GLASS.

| Range. Megabars. | Hg added. | Hg cor. 100–500 megabars. | Other data necessary. |
|---------------------|-----------|------------------------------|--------------------------|
| 99.0 — 503.7 | 0.2498 | 0.2470 | |
| 110.2 — 509.8 | 0.2478 | 0.2481 | |
| 102.7 — 503.5 | 0.2474 | 0.2471 | |
| 503.7 — 150.4 | 0.2171 | 0.2459 | W = 385.28 |
| 509.8 — 90.6 | 0.2580 | 0.2462 | D = 13.546 |
| 100.0 — 300.0 | (0.1256) | | |

Average = w = 0.2469

The difference between the compressibility of mercury and glass over the range from 100–500 megabars is 1.60, as calculated from the above results. Therefore, the compressibility of the glass must have been 2.35×10^{-6} . This is about the usual compressibility of soft glass.

It was necessary also in some cases, in order to prevent the substance from being attacked by the mercury, to surround the former with water—an expedient possible in both forms of piezometer, as may readily be seen. For this purpose it was needful to know exactly the difference between the compression of a gram of water and an equal bulk of mercury over the range 100–500 megabars; this was found to correspond to 0.2069 g. of added mercury, since 55.08 g. of water required 11.395 g. of added mercury, as a mean of many trials.

After these preliminaries, tables giving the data for the several other solid substances are now to be given.

TABLE IV.—OBSERVATIONS AND DATA CONCERNING THE COMPRESSIBILITY OF VARIOUS SOLIDS.

| Substance and conditions. | Pressure range. Megabars. | Weight mercury added. Grams. | Wt. mercury cor. to 100–500 megabars. Grams. | Other data necessary. $(\beta - \beta') \times 10^6$. |
|---|------------------------------|---------------------------------------|--|---|
| Copper under water and mercury in glass..... | 102.3–508.6 | 1.3463 | 1.3256 | $K = 6.971$ |
| | 508.6–103.2 | 1.3657 | 1.3268 | $m = 0.2069$ —318 |
| | 100.0–300.0 | (0.6837) | | $w' = 0.2469$ |
| | | | | $W = 187.368$ |
| | | | | $D = 8.894$ |
| Average = $w = 1.3262$ | | | | |

TABLE V.

| | | | | |
|---|-------------|----------|--------|-------------------|
| Copper under water and mercury in glass..... | 520.9–99.2 | 1.4345 | 1.3656 | $K = 7.190$ |
| | 99.2–517.2 | 1.4237 | 1.3652 | $m = 0.2069$ —321 |
| | 102.4–499.6 | 1.3565 | 1.3677 | $w' = 0.2469$ |
| | 95.5–503.4 | 1.3936 | 1.3670 | $W = 187.368$ |
| | 517.2–102.4 | 1.4121 | 1.3648 | $D = 8.894$ |
| | 100.0–300.0 | (0.7082) | | |
| Average = $w = 1.3661$ | | | | |

TABLE VI.

| | | | | |
|---|-------------|----------|--------|-------------------|
| Lead under water and mer- cury in steel..... | 111.3–501.6 | 4.3278 | 4.4441 | $K = 18.059$ |
| | 107.8–500.0 | 4.3487 | 4.4402 | $m = 0.2069$ —161 |
| | 102.3–501.5 | 4.4357 | 4.4468 | $w' = 1.0369^1$ |
| | 100.9–500.0 | 4.4348 | 4.4450 | $W = 426.67$ |
| | 100.7–500.8 | 4.4409 | 4.4423 | $D = 11.298$ |
| | 100.0–300.0 | (2.2807) | | |
| | 89.9–107.8 | (0.2105) | | |
| Average = $w = 4.4437$ | | | | |

¹ Before this experiment (which was chronologically the last made with the steel piezometer) the volume of the instrument had been somewhat diminished by turning off the shoulder receiving the washer, in order to make better contact.

TABLE VII.

| Substance and conditions. | Pressure range. Megabars. | Weight mercury added. Grams. | Wt. mercury cor. to 100-500 megabars. Grams. | Other data necessary. | $(\beta - \beta')$ $\times 10^4$. |
|---|------------------------------|---------------------------------------|--|--------------------------|---------------------------------------|
| Molybdenum under mercury in steel..... | 126.7-500.0 | 0.8927 | 0.9436 | $m = 0$ | |
| | 99.2-500.2 | 0.9464 | 0.9441 | $w' = 1.0384$ | —349 |
| | 100.6-501.1 | 0.9451 | 0.9440 | $W = 50.971$ | |
| | 100.0-300.0 | (0.4753) | | $D = 10.228$ | |
| | Average = $w = 0.9439$ | | | | |

TABLE VIII.

| | | | | | |
|---|------------------------|----------|--------|---------------|------|
| Tantalum under mercury in steel..... | 105.4-502.9 | 0.9965 | 1.0028 | $m = 0$ | |
| | 119.0-500.7 | 0.9573 | 1.0039 | $w' = 1.0384$ | —345 |
| | 102.7-504.9 | 1.0094 | 1.0041 | $W = 30.889$ | |
| | (100.0-300.0) | (0.5051) | | $D = 16.667$ | |
| | Average = $w = 1.0036$ | | | | |

TABLE IX.

| | | | | | |
|---|------------------------|----------|--------|---------------|------|
| Tungsten under mercury in steel..... | 104.5-499.8 | 0.9300 | 0.9412 | $m = 0$ | |
| | 104.4-502.3 | 0.9362 | 0.9415 | $w' = 1.0384$ | —368 |
| | 95.6-500.4 | 0.9551 | 0.9439 | $W = 91.676$ | |
| | 107.3-505.0 | 0.9387 | 0.9444 | $D = 19.231$ | |
| | 108.5-506.0 | 0.9382 | 0.9444 | | |
| | 100.2-501.2 | 0.9465 | 0.9445 | | |
| | 100.0-300.0 | (0.4746) | | | |
| | Average = $w = 0.9433$ | | | | |

TABLE X.

| | | | | | |
|--|------------------------|----------|--------|------------------|------|
| Tantalum with tungsten under mercury in steel.... | 98.2-499.5 | 0.9128 | 0.9101 | $K = 91.676$ | |
| | 119.2-501.1 | 0.8665 | 0.9092 | $m = -0.0010385$ | —336 |
| | 101.1-499.7 | 0.9038 | 0.9073 | $w' = 1.0384$ | |
| | 101.1-501.9 | 0.9127 | 0.9110 | $W = 30.889$ | |
| | 100.0-300.0 | (0.4575) | | $D = 16.667$ | |
| | Average = $w = 0.9094$ | | | | |

TABLE XI.

| | | | | | |
|--|------------------------|----------|--------|---------------|------|
| Silver bromide under water and mercury in glass.... | 103.0-494.9 | 2.1581 | 2.2032 | $K = 10.037$ | |
| | 494.9-111.4 | 2.1082 | 2.1990 | $m = 0.2069$ | —126 |
| | 102.7-500.7 | 2.1908 | 2.2027 | $w' = 0.2469$ | |
| | 500.7- 98.8 | 2.2123 | 2.2022 | $W = 115.965$ | |
| | | (1.1313) | | $D = 6.473$ | |
| | Average = $w = 2.2018$ | | | | |

TABLE XII.

| | | | | | |
|--|------------------------|--------|--------|---------------|------|
| Silver bromide under water and mercury in glass.... | 511.2- 91.9 | 2.2509 | 2.1476 | $K = 9.770$ | |
| | 99.4-510.7 | 2.2053 | 2.1480 | $m = 0.2069$ | —125 |
| | 99.9-499.4 | 2.1460 | 2.1492 | $w' = 0.2469$ | |
| | 103.9-499.6 | 2.1214 | 2.1459 | $W = 117.896$ | |
| | 499.4-103.9 | 2.1199 | 2.1445 | $D = 6.473$ | |
| | 510.7- 99.9 | 2.2015 | 2.1441 | | |
| | 100.0-300.0 | 1.1031 | | | |
| | Average = $w = 2.1465$ | | | | |

The data in the preceding tables yielded upon suitable calculation the following results, which represent the averages of all the determinations in each case. It should perhaps be noted that the two values for $\beta - \beta'$ for tantalum, -3.45×10^{-6} and -3.36×10^{-6} are the most widely discrepant of all the values. This was doubtless because so small a quantity of tantalum was used—less than 2 cc. The first (more directly found) value may be given twice the weight of the second. In the case of copper on the other hand, where two entirely separate sets of observations were made, the values for $\beta - \beta'$ were, respectively, 3.18×10^{-6} and 3.21×10^{-6} . In both cases study of the data will show that this agreement is as good as could reasonably be expected, considering the quantities of materials used and the extremely minute values to be measured.

Attention is called to the extremely small value of the compressibility of tungsten—the smallest, perhaps, of any substance which has thus far been measured.

FINAL RESULTS.

Temperature = 20.0°.

Calculated upon the megabar standard.

| Substance. | $(\beta - \beta') \times 10^6$. | Compressibility $\times 10^6$. (Average over range 100–500 megabars.) |
|----------------------|----------------------------------|--|
| Copper..... | —3.20 | 0.76 |
| Iron (standard)..... | —3.35 | (0.61) |
| Lead..... | —1.61 | 2.35 |
| Mercury..... | 0 | 3.96 |
| Molybdenum..... | —3.49 | 0.47 |
| Tantalum..... | —3.42 | 0.54 |
| Tungsten..... | —3.68 | 0.28 |
| Silver bromide..... | —1.26 | 2.70 |

It will be seen that the values given in the first column of figures agree quite as closely as could be expected with the values given for $\beta - \beta'$ by the early Harvard work. Thus the old value for copper was -3.25 ;¹ that for iron -3.385 ; that for lead (only a single experiment) -1.55 ; and that for silver bromide -1.20 , all reduced to the megabar standard. The reason why the compressibilities formerly computed from these values differed considerably from those in the last column above is simply because β' was taken as 3.79×10^{-6} in the old work (the best value then available), whereas in the present work it is taken as 3.96×10^{-6} —a difference of 0.00000017, which must be added to all the old values in order to make them correspond to the present knowledge concerning mercury. A more extensive discussion of this connection will be given in another place.

It is interesting to note also that the values given above are in excellent accord with the results of Grüneisen, as indicated in the papers already mentioned. His average value for copper is 0.74 to 0.78; for iron 0.59

¹ *Pub. Carnegie Inst. Wash.*, 76, 44 (1907).

to 0.64; for lead (which is too soft to give good results by his method), 2.0 to 3.2. Thus in each case our values lie between his extremes. The other substances were not studied by him, and there are two among them (namely, tantalum and tungsten) which have never before had their compressibilities determined, so far as we know. It is especially satisfactory to have the apparent inconsistencies of the earlier results adequately explained and removed.¹

We are greatly indebted to the Carnegie Institution of Washington for generous support in this investigation.

Summary.

This paper describes careful determinations involving the compressibilities of eight substances, of which two had apparently never been studied before, namely, tantalum and tungsten. The method which has been used for over ten years by one of the authors was modified by the construction of the piezometer of steel instead of glass. This change has the advantage of avoiding the hysteresis of glass under high pressure. The results show, however, that the method of manipulation used in the earlier work had overcome this difficulty and that the earlier results were quite as satisfactory and accurate as they were supposed to be at the time. The difference in the final values of the compressibilities is due chiefly to the change in the assumed compressibility of mercury, which is now referred to a better new absolute value for iron (0.00000061) rather than to earlier less accurate work. The compressibility of the various substances, at 20° (expressed in the megabar standard, multiplied by a million) were found as follows: Copper 0.76, lead 2.35, mercury 3.96, molybdenum 0.47, tantalum 0.54, tungsten 0.28, silver bromide 2.70. In each case the range of pressure was between 100 and 500 megabars. The outcome is as consistent as could be expected with the work of Bridgman and Grüneisen, and previous discrepancies are explained. Especial attention is called to the very small compressibility of tungsten.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY OF THE CARNEGIE INSTITUTION.]

THE MEASUREMENT OF THE FREEZING-POINT DEPRESSION OF DILUTE SOLUTIONS.

By LEASON H. ADAMS.

Received December 20, 1914.

The present paper is a description of a method of determining the freezing-point depression of dilute solutions, by the use of which one is enabled to observe the equilibrium temperature with an uncertainty

¹ Attention is called to the interesting compilation by W. Schut entitled "Piëzo-chemie der Gecondenseerde Systemen" (Utrecht, 1912) when some of these matters are discussed.

no greater than 0.0001° and to measure the equilibrium concentration with commensurate accuracy. Results are presented for the non-electrolyte mannite and for the salts KCl and KNO_3 , all at concentrations ranging from about 5 to 100 millimolal; the latter are shown to agree very well, at the lowest concentrations, with the degree of ionization derived from conductance measurements.

The characteristic property of an electrolyte in aqueous solution is its degree of ionization, or its mol number; the latter, which is directly related to the former, is the relation of the apparent concentration—as deduced from the freezing point (or vapor pressure or osmotic pressure) of the solution by means of the laws of the perfect solution—to the concentration calculated on the basis of the respective weights of solute and solvent present. The mol-number may also be derived from the conductance ratio, on the basis of certain assumptions, of which the most important are: (1) that the equivalent conductance (Λ_0) of the ions does not vary with the concentration, except in so far as the fluidity of the solution varies; (2) that an accurate value of Λ_0 can be obtained by extrapolation from the measured conductances, and that the influence of change of fluidity upon this Λ_0 value can be satisfactorily allowed for. The usual interpretation of the results obtained from any of the methods of measurement involves the assumption that the only forms in which the substance exists in the solution are the un-ionized molecules and the ultimate simple ions into which they dissociate at extreme dilution.¹

Altogether then, the mol-numbers derived from the conductance ratio are trustworthy only when the uncertainties involved in the above assumptions are unimportant—in other words, only when the concentration is as small as 0.1 formal, or even less. Of the other methods, the one susceptible of the highest accuracy at the present time is the measurement of the freezing-point depression; but unfortunately it is a matter of some difficulty to measure the freezing point of such dilute solutions with sufficient percentage accuracy to admit of a really satisfactory comparison of the mol-numbers so derived with those derived from the conductance of such solutions. For example, a 0.01 formal solution of KCl freezes at -0.0361° , so that an error of only 0.001° in the equilibrium temperature corresponds to an error of 3% on the observed lowering, and accordingly to an uncertainty of 6% in the degree of ionization derived therefrom; while further uncertainty will of course result if the concentration of the solution in equilibrium with ice at the freezing point is not known with sufficient accuracy—and lack of exactness in this respect has been a frequent source of error in the past. But for a trustworthy comparison of the mol-numbers derived in the two ways, the degree of ionization derived

¹ With regard to these matters, see especially A. A. Noyes and K. G. Falk, *This Journal*, 32, 1011-15 (1910); 34, 454-60, 487-9 (1912).

from the freezing point should be known within 1%, even for the solutions ranging down to 0.005 formal; this degree of accuracy necessitates the determination of the freezing-point depression to 0.0001° , and a commensurate exactness in the equilibrium concentration. A method of achieving this accuracy is presented in the following pages; but before describing it, we shall refer briefly to some of the best recent work in this field.

During recent years the determination of the freezing-point depression of aqueous solutions has been undertaken by a large number of investigators, with a steady improvement in apparatus and technique. The principal improvements are two: the substitution of a device for measuring directly the depression of freezing point, in place of the mercury thermometer which measured the freezing point only and that with a precision probably not better than 0.001° ; the abandonment of the old Raoult method of supercooling a solution of known concentration, which involved a correction for change of concentration due to separation of ice, as well as an uncertainty in the equilibrium temperature.

As a temperature-measuring device for accurate work, mercury thermometers were abandoned in favor of compound thermoelements by Hausrath,¹ Osaka,² Jahn,³ and Flügel;⁴ also by Bedford,⁵ who employed a differential platinum resistance thermometer. The first one to improve on the original Raoult supercooling method was Roloff,⁶ who, acting upon a suggestion of Nernst, determined by analysis the composition of solutions in equilibrium with a large amount of ice which had been frozen out of the solutions. Jahn,⁷ Flügel,⁴ and Roth⁸ later made use of this same method, while Walker and Robertson,⁹ and also Richards¹⁰ mixed the salt solutions directly with ice separately frozen and placed in the freezing-point vessel. This last procedure is to be preferred because it minimizes the chance of error from a possible solubility or inclusion of the salt in the ice.

The data of Jahn and of Flügel are probably the most generally reliable, but even they are not entirely beyond question; because, so far as one can gather, neither investigator appreciated the importance of homogeneity in wire used for thermocouples or of the necessity of special tests for, and

¹ H. Hausrath, *Ann. Physik*, [4] 9, 522 (1902).

² Y. Osaka, *Z. physik. Chem.*, 41, 560 (1902).

³ H. Jahn, *Ibid.*, 59, 31 (1907).

⁴ F. Flügel, *Ibid.*, 79, 577 (1912).

⁵ T. G. Bedford, *Proc. Roy. Soc. London*, (A) 83, 454 (1910).

⁶ M. Roloff, *Z. physik. Chem.*, 18, 572 (1895).

⁷ H. Jahn, *Ibid.*, 50, 129 (1905); 59, 31 (1907).

⁸ W. A. Roth, *Ibid.*, 79, 599 (1912).

⁹ J. Walker and A. J. Robertson, *Proc. Roy. Soc. Edinburgh*, 24, 363 (1902).

¹⁰ T. W. Richards, *Z. physik. Chem.*, 44, 563 (1903); *THIS JOURNAL*, 25, 291 (1903).

the removal of, the heterogeneous portions of the wire so used. It is also open to question whether their respective potentiometer outfits were of a type sufficiently free from parasitic electromotive forces to insure the accurate reading of small fractions of microvolts. In other words their temperature measurements may not be so accurate as the published data would suggest. This matter will be reverted to later.

The Method.—The essentials of accurate freezing-point determinations are substantially as follows: (1) Rapid and certain attainment of a (practically) stationary temperature equilibrium; (2) accurate and convenient measurement of the temperature, preferably of the freezing-point lowering directly by means of a differential method; (3) determination with sufficient exactness of the concentration of the equilibrium solution. These conditions were realized: (1) by thoroughly mixing the solution with a large amount of broken ice by means of a specially designed stirrer; (2) by measuring directly, with a multiple-junction thermoelement and sensitive potentiometer outfit, the difference between the equilibrium temperatures, ice-solution and ice-water; (3) by analyzing the equilibrium solution by means of a Zeiss interferometer¹ used practically as a zero instrument. We shall now proceed to describe the apparatus in detail.

Temperature Measurement.

The Thermoelement.—Copper and constantan were selected as the thermoelectric pair since in magnitude of thermoelectric power, homogeneity, permanence, and ready availability this is, at present, the most generally suitable couple for use at low temperatures. The copper wire used was No. 36 B. S. (0.15 mm.), the constantan No. 30 (0.25 mm.) both double silk covered.² The element was made up of 50 couples connected in series and all enclosed at each end in a single glass tube of about 7 mm. outside diameter.

Construction of the Element.—Full details of construction are presented since they may be useful to any one desiring to make a similar element. From a sufficient length of copper, and of constantan wire which had been carefully tested for homogeneity,³ the 50 pairs of wires were cut off and covered with shellac; when dry they were bared of insulation for 2 or 3 mm. at each end, and hard-soldered together as shown

¹ In the case of electrolytes the electrical conductance could well be employed as a means of determining the equilibrium concentration.

² The "Ideal" wire made by the Electrical Alloy Co., Morristown, N. J., is the best constantan wire for thermoelements which we have used. Almost any copper wire will be found suitable. Instead of silk-covered wire the enameled wires now obtainable possess certain advantages, namely that the insulation is thinner and will stand more handling and a higher temperature without deteriorating.

³ See W. P. White, *THIS JOURNAL*, 36, 2296 (1914). The most convenient method of testing a small lot of wire is to draw it through a narrow U-tube, preferably of metal, immersed in boiling water. It is not necessary to test the copper wire.

diagrammatically in Fig. 1, care being taken that the finished joints are free from sharp points or projections.

The best method of hard-soldering such small wires is to use a tiny gas flame (8 mm. long) issuing from a glass tip with a hole 0.2 mm. in diameter at the end; the solder consists of a mixture of 3 parts of brass to 1 of silver, and (anhydrous) borax glass is used as a flux. The whole operation is rapid and easy if one is careful to use small quantities of both borax and solder—not more than 0.5 mg. of borax and 3 mg. solder for each joint.

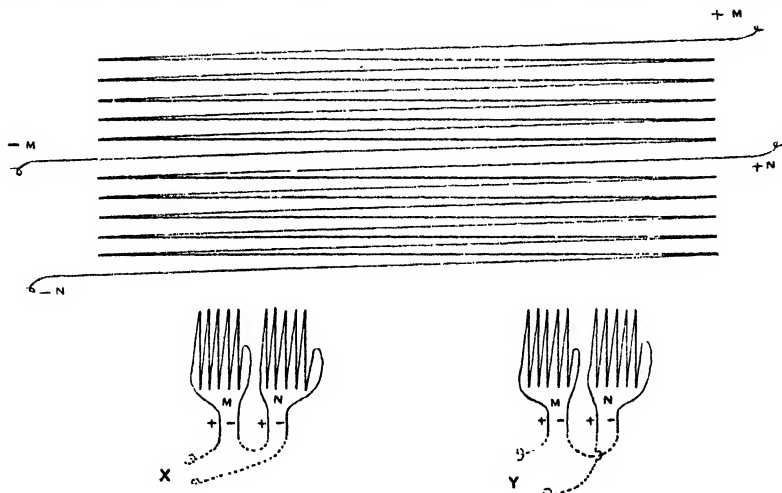


Fig. 1.—Diagram to show arrangement of the copper and constantan wires in the thermoclement. The wires are joined in two groups of 5 couples (25 in the actual element); the terminal (copper) wires of which may be connected either as at X or at Y, thus enabling one to throw the two halves either in series or in opposition.

When soldered the junctions are covered with an insulating varnish of which the best is a coating of hard rubber applied as follows: Enough precipitated sulfur, or still better insoluble sulfur, is stirred up with rather thick rubber cement (pure gum rubber dissolved in benzene and carbon disulfide) to equal 20–25% of the solid rubber. The junctions are dipped in this mixture and, after drying in the air, maintained at 140° for 15 hours or longer.

The element is now ready to be assembled and enclosed. As may be seen from Fig. 1 the wires are joined together in two halves with four lead-wires, by means of which the two halves may be connected either in series or in opposition. This arrangement allows the element to be tested at any time for electrical leaks or short circuits, since if one end is placed in ice while the other end remains at room temperature, the electromotive force at Y (Fig. 1) will be zero only when there are no internal short circuits or leaks. Measurement of the resistance of the two halves and of

the insulation resistance¹ between them will serve the same purpose and is especially useful during the final assembling and enclosure of the wires. Experience has demonstrated the necessity of constantly testing in this way the element at all stages of construction in order to detect and obviate all internal leaks or short circuits.

In binding the wires together it is desirable to distribute the junctions in the form of a cone about 4 cm. long and to make a compact bundle of the wires by wrapping with fine silk thread. The necessary stiffness in the central portion is secured by binding in a small brass rod, bent to shape, extending about 3 cm. beyond each bend. Each end is embedded in fused naphthalene in a glass tube of as small diameter as practicable; and finally the central portion is paraffined (in order to exclude moisture, which may cause the insulation resistance to decrease beyond the margin of safety) and wrapped with silk ribbon. It is advisable to protect the lead-wires from possible breakage, especially at their point of exit, by twisting them together with a thin piece of cord.

Potentiometer.—A potentiometer² of careful design was used, by means of which, in conjunction with a sensitive Weston galvanometer, a precision of 0.1 microvolt was readily attained. The whole potentiometric apparatus was protected from leakage, etc., by two equipotential shields,³ so that even in damp weather the total leakages and parasitic electromotive forces never exceeded 0.5 microvolt. The residual leakage, etc., was, however, continuously compensated for by means of the usual eliminating switch. The lowest decade consisted of steps of 10 microvolts each; units and tenths of microvolts were read directly with telescope and scale, the sensitiveness of the galvanometer being kept adjusted so that 10 microvolts gave a deflection of exactly 10 divisions on the scale.

Calibration of the Element.—The thermoelement was calibrated against a 24-junction element previously calibrated at the Bureau of Standards to 0.001° between 0° and 50°. Comparisons with the standard element were made in a well-stirred kerosene bath at 10°, 20°, and 30°; from these readings an equation was calculated which expresses the relation between the temperatures as determined by the standard element and the microvolts registered by the unknown element.⁴ By differentia-

¹ It is convenient to do this on the potentiometer itself.

² This potentiometer has been described by W. P. White in *Z. Instrumentenkunde*, 34, 79 (1914).

³ A full discussion of choice of potentiometers, mode of shielding, and other points in connection with potentiometer installation, is given in recent papers by W. P. White, *THIS JOURNAL*, 36, 1856, 1868, 2011 (1914).

⁴ The readings of a copper-constantan couple at these low temperatures are reproduced equally well by a cubic equation of the form $E = At + Bt^2 + Ct^3$ and by an exponential of the form $E = At + B(1 - e^{Ct})$. At higher temperatures the latter is preferable. Compare L. H. Adams, *J. Wash. Acad. Sci.*, 3, 469 (1913).

tion of this equation, the gradient at 0° —that is the number of microvolts per degree at 0° —was derived. This gradient changes by only $1/400$ of itself per degree, and therefore small temperature differences may be accurately obtained from the readings in microvolts simply by multiplying by the reciprocal of the gradient—in the present instance 0.0005198° per microvolt at 0° . As the temperature difference increases, however, the departure from linearity becomes appreciable, being proportional to the square of the temperature difference; thus at temperatures of -0.3° , -0.4° and -0.5° the error introduced by the assumption of strict linearity is 0.0001° , 0.0002° and 0.0003° , respectively. The temperatures obtained by multiplying the reading in microvolts by the factor above mentioned have been corrected, therefore, by adding the appropriate small amount.

Freezing-point Apparatus.—The freezing-point vessels consist essentially of two exactly similar vacuum jacketed silvered jars *A* and *B* (Fig. 2), arranged so that they are completely surrounded by melting ice. One end of the thermoelement dips into *A*, which contains ice and water, the other into *B*, which contains ice and solution; thus, by means of this arrangement the thermoelement records directly the freezing-point lowering produced by the salt. Each jar is closed with a cork-stopper, previously thoroughly soaked in hot paraffin, which serves also to hold the thermoelement and pipet in position. The jars sit in cylindrical tin cans, which are supported in a large sheet metal pot, covered with a thick layer of wool felt, and nearly filled with ice. The double lid, likewise covered on the top with felt, is also filled with ice. This arrangement secures the great advantages: (1) that the maximum temperature gradient to which the thermoelement is exposed does not exceed 1° ; (2) that the melting of the ice, and consequently the change of concentration of the solution, and hence of freezing point, is very slow. Indeed the freezing point of the solutions, even when left unstirred, did not change by more than 0.001° in an hour.

Mode of Stirring.—Thorough admixture of solution with the ice is absolutely essential; this is secured by the similar stirrers *S*, *S*, which are shown more in detail in Fig. 3. This stirrer is really a circulating pump, its function being to withdraw liquid from the bottom of the vessel and discharge it over the top of the ice, whence it flows downward through the ice to the bottom again; relatively few strokes are sufficient for the attainment of complete mixing and cooling. The pump is of brass, heavily gold plated. The barrel *E* (Fig. 3) is a half cylinder open at both ends except for the screen at the bottom which serves to prevent ice from entering the stirrer; this barrel is held in position in the freezing vessel by means of the thin strips *H* which act as springs. The bucket-shaped piston *D*, which is a fair fit for the inside of the barrel, is moved up and

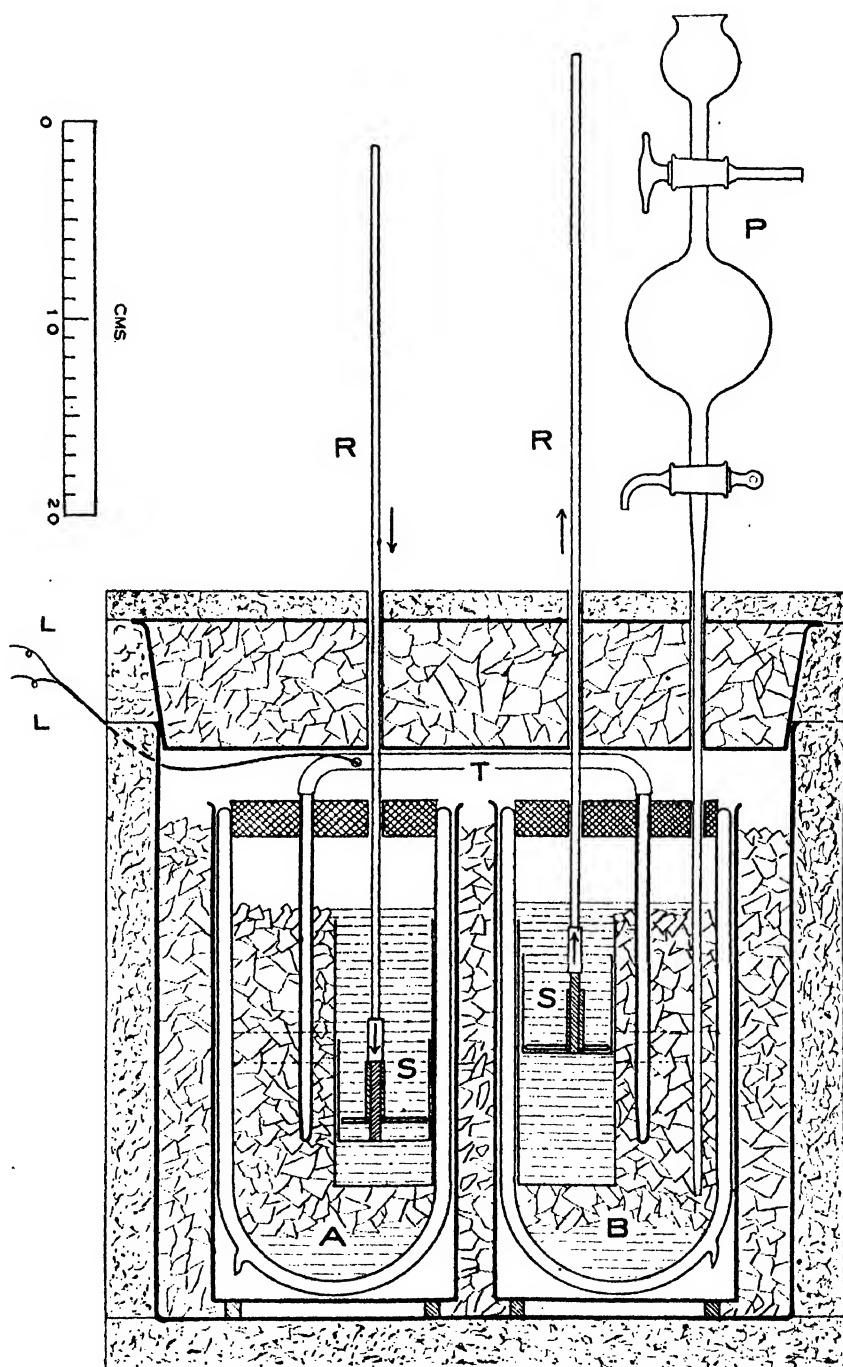


Fig. 2.—Freezing-point apparatus. Two exactly similar vacuum-jacketed vessels (A, B) are surrounded with cracked ice contained in a large pot which is well insulated by a layer of wool felt. The double lid is also filled with ice and covered with felt. Jar A contains finally about 400 g. ice and 600 g. water; jar B the same respective amounts of ice and solution. The liquid in each jar is stirred by means of the similar hemicylindrical stirrers S, S which, when actuated by the glass rods R, R, pump liquid from the bottom of each jar and discharge it at the top over the ice. The difference in temperature between ice-water and ice-solution is measured directly by the differential thermoelement of 50 junctions and sensitive to 0.0001° . Two thermoelement lead-wires (there are really four) are shown at L, L. When temperature equilibrium is attained a sample for analysis is withdrawn by means of the combined pipet and funnel P, which also serves to introduce water and solute into jar B. When equilibrium is attained in both A and B, the temperature difference to 0.0001° is measured directly by means of the 50-junction differential thermoelement (T; its terminal wires are L, L); the concentration is determined on a sample withdrawn through the pipet P.

down by means of a glass rod fastened to the central stem, G; it is open at the top, and its bottom is slotted as shown in the figure. These open

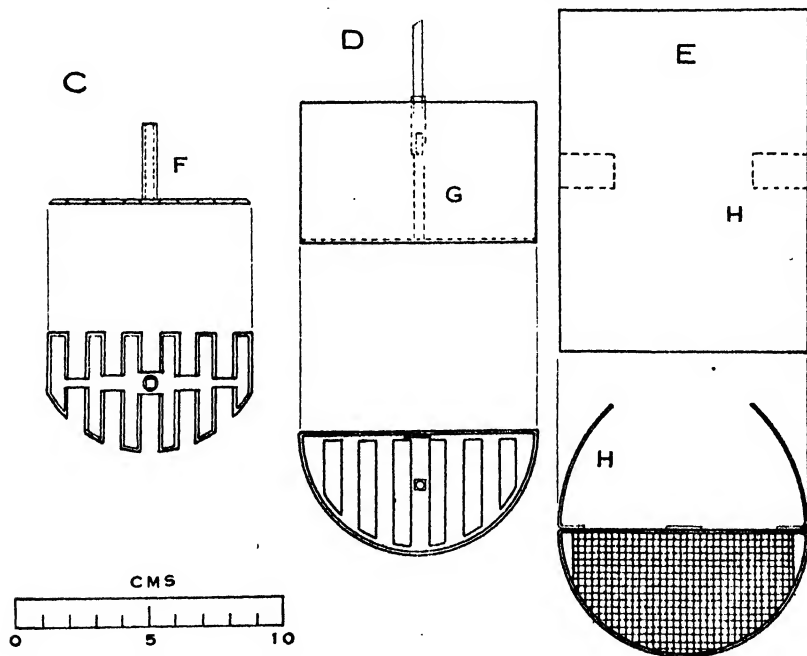


Fig. 3.—Drawing in plan and elevation of stirrer; to show mode of operation. The stirrer, made of brass heavily gold-plated, is really a circulatory pump with a hemicylindrical barrel. In this barrel, E, open at both ends, the bucket-shaped piston D slides easily; D is open at the top and slotted at the bottom, the slots being closed by the clapper C when D is raised, but open when D is lowered. The clapper C is kept in alignment by the bearing F which slides on the square stem G. The stirrer is operated by means of the glass rod R (Fig. 2), and held in place in the freezing-point vessel by the springs H, H.

spaces are just covered by the solid portions of the clapper-valve *C* which is held in alignment by the small hollow barrel *F* sliding on the stem *G*. *It is thus evident that when the bucket with clapper in place is pushed down through liquid contained in the barrel, the pressure of the liquid from below will force the clapper to rise and allow liquid to flow through; but when the bucket is raised the clapper is held down, and hence liquid is lifted up and out over the top of the barrel. The piston was made bucket-shaped in order to avoid any considerable leak and to have at the same time a loose and easy fit. These stirrers proved to be very efficient; each stroke circulated approximately one-half of the liquid in the vessel, and consequently but little stirring was required.*

Analysis of the Equilibrium Solution.—Samples for analysis were withdrawn by means of the sampling pipet *P*, which served also for the addition of water or of solute (in the form of a concentrated cooled solution). The concentration of the solutions was determined by what is practically a zero method; namely, a Zeiss interferometer was used to compare this unknown solution with known solutions of very nearly the same concentration, and hence served practically as a means of interpolation over a small range. In the case of mannite a series of known solutions was compared with water, and the readings plotted; the unknown solutions were also compared with water and their concentration was derived by interpolation on this curve of the readings of the instrument. The former way is in general preferable, since there is then less chance of mistaking the proper band for comparison.

With the instrument used in this work¹ one can bring the upper and lower bands into conjunction with an uncertainty of not more than 1 division on the scale. It is thus possible, with the 40 mm. chamber, to determine the percentage composition of a solution of a colorless salt or non-electrolyte to within 0.0002—that is to within two parts of salt in a million of water. The attainment of this degree of certainty demands some experience with the instrument; this matter will not be discussed further here, since it forms the subject of another communication.

Experimental Procedure.—The vacuum-jacketed jars are set in position in the large can and surrounded by cracked ice; the stirrers are set in place and about 500 cc. of cooled distilled water poured into each jar. Ice,² in pieces about the size of an almond and previously washed with distilled water, is then put into each vessel until the half not occupied by the stirrer is filled; this required about 500 g. The water level is then adjusted so as to be about 5 mm. above the top of the stirrer. The para-

¹ The Water Interferometer manufactured by Carl Zeiss, Jena.

² Ordinary artificial ice was used. This ice was always very pure, being made from distilled and filtered water. Moreover, as will be explained below, any small residual impurity in the ice would be without prejudicial effect on the final results.

finer cork stoppers are then placed on the jars, one leg of the thermoelement pushed into each jar and the ice-filled cover placed in position¹ on the outer can. The narrow tube of the sampling pipet is then shoved through a hole in the cover and down into jar *B*.

The apparatus is then allowed to stand for two or three hours with occasional stirring in order that all the various parts in the interior may cool down to nearly zero; after which both sides are stirred until a constant thermoelement reading is obtained. This so-called "zero" reading² is noted, and a sample of about 50 cc. withdrawn from jar *B* and preserved in a Jena glass flask sealed with a sheet of tinfoil tightly crimped about the neck of the flask. The purpose of this initial sample is to determine a "concentration zero" reading on the interferometer. The desired amount of solute dissolved in enough ice-cold water to make up the exact volume of liquid previously withdrawn is then added; both sides are again stirred at intervals until temperature equilibrium is attained. In order to rinse the pipet *P*, it is half filled with solution by suction and given a gentle rotary shake, after which process the solution is returned to the vessel. A few strokes of the stirrer suffices to bring about a condition of equilibrium which, with occasional stirring, does not change in the course of several minutes. The temperature is now read and a sample of 50 cc. for analysis withdrawn by means of the pipet *P*. More salt may now be introduced for a new determination. From each temperature reading the "zero" temperature reading is subtracted and similarly from each concentration reading is deducted the "zero" concentration reading—that is, the reading on the interferometer of the zero sample against the water from which the standard calibration solutions were made up.

Usually a series of five or six determinations was carried out with one set-up of the apparatus; but it is to be noted that the several pairs of readings constitute a series of independent observations. That there is no serious systematic error follows from the smallness and constancy of the two zero readings; moreover, any factor prejudicial to the result would have increased *both* of these readings and hence would be substantially eliminated. Nevertheless, it was thought desirable to have a direct check on the accuracy of the method; for this purpose a series of determinations were made with dilute solutions of the non-electrolyte mannite. These results, together with those obtained with the salts potassium nitrate and potassium chloride, will now be presented.

¹ This was facilitated by guiding rods (not shown in Fig. 2).

² This reading was usually about 1 microvolt, but probably does not indicate a corresponding difference in temperature (0.0005°) between the two vessels. It undoubtedly represents the summation of several small electromotive forces. The analogous concentration "zero" reading was never greater than 3 divisions on the interferometer.

Experimental Results.

Mannite.—The mannite was recrystallized from water and dried by heating *in vacuo* for several hours at 130°. Table I is a complete record of the observations. The first three columns reproduce (I) the measured equilibrium concentration ($N \times 10^3$), expressed in millimols per 1000 g. of water, and the directly measured freezing-point depression (II) in microvolts and (III) in degrees. The fourth column shows the calculated lowering as derived from the equation $N = \Delta t (1 + 0.0055\Delta t)/1.858$, the theoretical expression for the depression of a solution containing N moles per 1000 g. of water; the fifth gives the differences, in ten-thousandths of a degree, between the observations and the values so calculated. The last two columns are a similar comparison of the observed concentration with that calculated from the observed depression.

The differences are in no case greater than 0.0001°, and thus justify our expectations as to the accuracy of the method.

TABLE I.—FREEZING-POINT DEPRESSIONS PRODUCED BY MANNITE IN DILUTE AQUEOUS SOLUTION.

| I. Concentration millimols per 1000 g. H ₂ O. $N \times 10^3$. | II. F.-p. depression. Δt (obs.). | | IV. Δt (calc.). | V. Diff. obs.-calc. 10 ⁻⁴ degrees. | VI. $N \times 10^3$ calc. | VII. Diff. obs.-calc. Millimols. |
|--|--|----------|----------------------------|--|---------------------------------|---|
| | $\mu v.$ | Degrees. | | | | |
| 4.02 | 14.4 | 0.0075 | 0.0075 | 0 | 4.04 | —0.02 |
| 8.42 | 30.3 | 0.0157 | 0.0156 | 1 | 8.45 | —0.03 |
| 14.04 | 50.0 | 0.0260 | 0.0261 | —1 | 13.99 | 0.05 |
| 28.29 | 100.9 | 0.0525 | 0.0525 | 0 | 28.26 | 0.03 |
| 62.59 | 223.5 | 0.1162 | 0.1162 | 0 | 62.58 | 0.01 |

Potassium Nitrate.—This salt was chosen for the reason that, as shown in the compilation of Noyes and Falk,¹ there is a large discrepancy between the ionization values of KNO₃, as determined by the two methods of freezing-point lowering and conductance ratio.

The salt used was twice recrystallized from H₂O and dried by heating *in vacuo* at 150° for several hours. The results are given in Table II.

TABLE II.—FREEZING-POINT DEPRESSIONS PRODUCED BY KNO₃ IN DILUTE AQUEOUS SOLUTION.

| I. Concentration formula-weights per 1000 g. H ₂ O. N . | II. Δt . | | IV. $\Delta t/N$. |
|--|---------------------|----------|-----------------------|
| | $\mu v.$ | Degrees. | |
| 0.00443 | 30.9 | 0.0161 | 3.63 |
| 0.00817 | 56.8 | 0.0295 | 3.61 |
| 0.01565 | 107.4 | 0.0558 | 3.565 |
| 0.03874 | 258.3 | 0.1343 | 3.467 |
| 0.05766 | 377.1 | 0.1960 | 3.399 |
| 0.12270 | 772.4 | 0.4017 | 3.274 |

The first column exhibits the measured concentration (N), in formula-weights per 1000 g. water, the second and third the observed depression

¹ Noyes and Falk, THIS JOURNAL, 34, 485-9 (1912).

in microvolts and degrees, respectively; the last column contains the several values of $\Delta t/N$, the formal lowering. The concordance between the several observations is shown in Fig. 4, in which the formal lowering is plotted against $\log 10^3 N$; the dotted lines above and below the curve indicate the distance through which the curve would be displaced in either

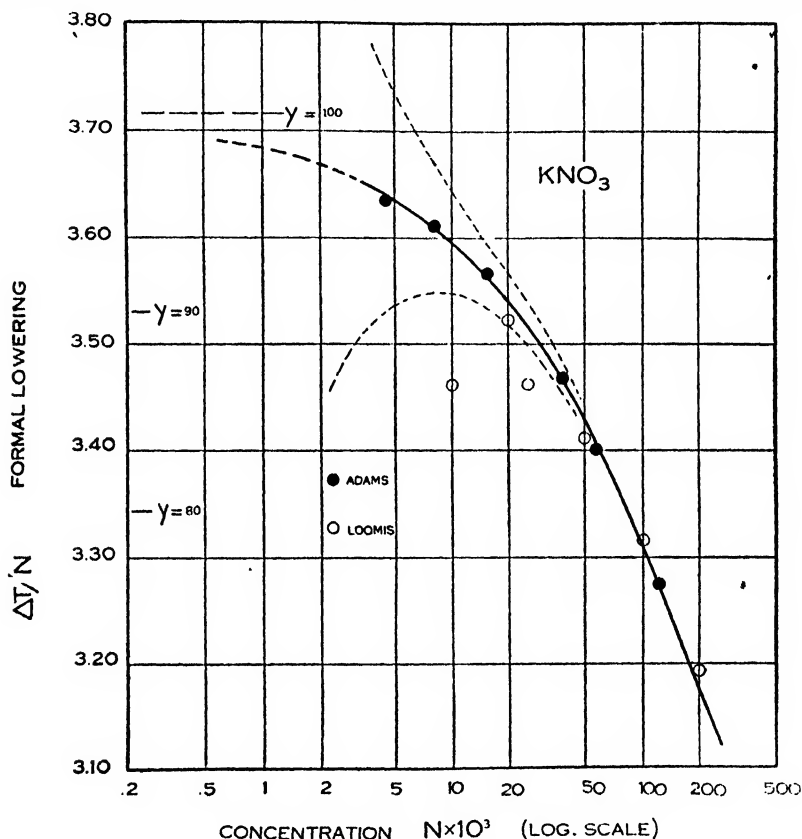


Fig. 4.—Observations on the freezing-point depression produced by KNO_3 in dilute solution. The dotted lines above and below the curve represent the displacement of the curve which would be caused by an error of $\pm 0.0005^\circ$.

direction by an error of 0.0005° . For the sake of comparison the data of Loomis² are also included; his results are in general too low, as Noyes and Falk³ presumed. The recent measurements of Roth,⁴ made by a method identical with that used by Loomis, are so numerous that they

¹ This diagram was actually plotted on coördinate paper having a logarithmic scale in one direction.

² E. H. Loomis, *Ann. Physik*, **57**, 504 (1896).

³ Noyes and Falk, *THIS JOURNAL*, **32**, 1017 (1910).

⁴ W. A. Roth, *Z. physik. Chem.*, **79**, 599 (1912).

could not well be included in the diagram; Roth's data lie very close to those of Loomis and are, therefore, presumably affected by a similar error.

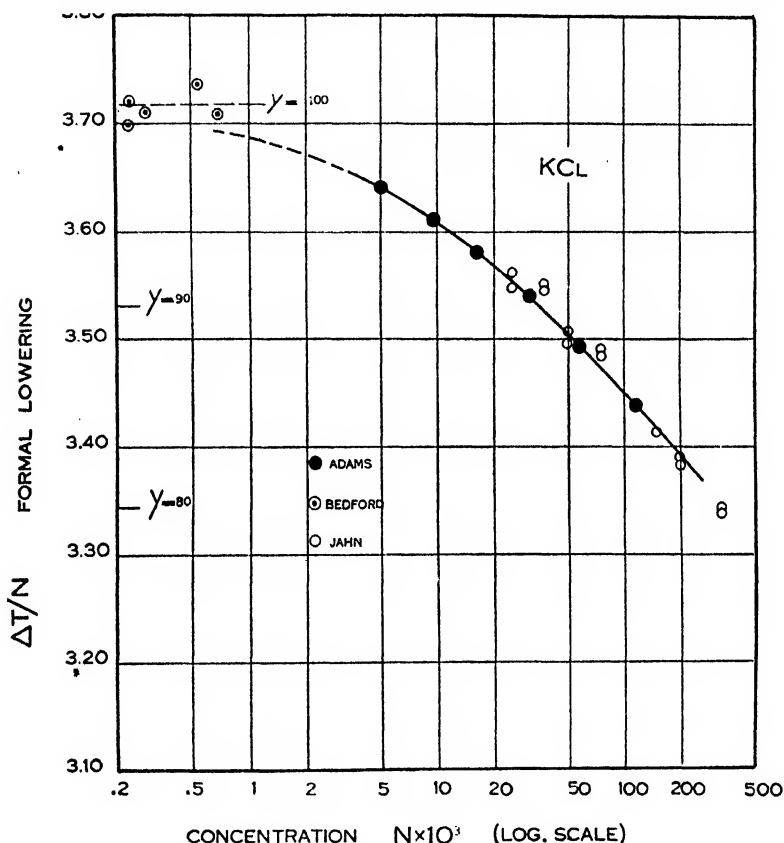


Fig. 5.—Observations on the freezing-point depression produced by KCl in dilute solution.

Potassium Chloride.—This salt was twice recrystallized from H_2O , dried first *in vacuo* and then ignited in a platinum dish at a temperature

TABLE III.—FREEZING-POINT DEPRESSIONS PRODUCED BY KCl IN DILUTE AQUEOUS SOLUTION.

| I Concentration formula-weights per 1000 g. H_2O . N . | II. | III. | IV. $\Delta T/N$. |
|--|----------|----------|-----------------------|
| | $\mu v.$ | Degrees. | |
| 0.00506 | 35.4 | 0.0184 | 3.64 |
| 0.00963 | 67.0 | 0.0348 | 3.61 |
| 0.01648 | 113.5 | 0.0590 | 3.580 |
| 0.03170 | 215.9 | 0.1122 | 3.539 |
| 0.05818 | 390.7 | 0.2031 | 3.491 |
| 0.11679 | 771.8 | 0.4014 | 3.437 |

just below its melting point. The observations are brought together in Table III and plotted in Fig. 5, in which are also included the data of Jahn¹ and Bedford² on this salt.

Discussion of Results.—From the observations tabulated in Tables II and III values of the formal lowering at round concentrations were obtained by graphic interpolation; these are presented in Table IV. The first column contains the concentration (N); the second, the corresponding formal lowering; the third, the mol-number (i) as calculated from the equation $i = \Delta t (1 + 0.0055\Delta t)/1.858 N$, and the fourth, the corresponding percentage ionization γ as derived from the relation $\gamma = 100(i - 1)$.

The ionization values in Cols. V and VI are taken from the paper of Noyes and Falk;³ they are derived, respectively, from the conductance-viscosity ratio and from the weighted means of the freezing-point data on these salts available in 1910.

TABLE IV.—FORMAL LOWERINGS AT ROUND CONCENTRATIONS, AND THE DERIVED MOL.-NUMBERS AND IONIZATION VALUES; COMPARISON WITH THE CONDUCTANCE RATIO.

| KNO ₃ . | | | | | |
|--|---|----------------------------------|--|----------------------------|--------------------------------------|
| I. Concentration formula-weights per 1000 g. H ₂ O. N . | II Formal lowering, $\Delta t/N$. | III. Mol. number, i . | Ionization value γ derived from | | |
| | | | f. p. (Adams). | Conduc- tance ratio. | f. p. weighted mean. (N. & F.) |
| 0.002 | 3.656 | 1.967 | 96.7 | 97.0 | |
| 0.005 | 3.638 | 1.958 | 95.8 | 95.3 | |
| 0.01 | 3.599 | 1.937 | 93.7 | 93.5 | 90.1 |
| 0.02 | 3.544 | 1.908 | 90.8 | 91.1 | 88.0 |
| 0.05 | 3.431 | 1.848 | 84.8 | 86.7 | 83.6 |
| 0.1 | 3.314 | 1.787 | 78.7 | 82.4 | 78.1 |
| KCl. | | | | | |
| 0.002 | 3.658 | 1.968 | 96.9 | 97.1 | |
| 0.005 | 3.643 | 1.961 | 96.1 | 95.6 | 96.3 |
| 0.01 | 3.609 | 1.943 | 94.3 | 94.1 | 94.3 |
| 0.02 | 3.570 | 1.922 | 92.2 | 92.2 | 91.8 |
| 0.05 | 3.505 | 1.888 | 88.8 | 88.9 | 88.5 |
| 0.1 | 3.451 | 1.861 | 86.1 | 86.0 | 86.1 |

Comparison of Cols. IV and V shows that in the case of potassium nitrate the difference between the ionization derived from freezing point and from conductance is no greater than the experimental error at all concentrations up to 0.02 molal; this disposes of the discrepancy noted by Noyes and Falk, whose mean values for this salt are derived solely from Loomis' data which, as they considered probable, are too low. At the higher concentrations the values in Cols. IV and V diverge; this shows merely

¹ H. Jahn, *Z. physik. Chem.*, 50, 137 (1905).

² T. G. Bedford, *Proc. Roy. Soc. London*, (A) 83, 454 (1910).

³ Noyes and Falk. *THIS JOURNAL*, 34, 486 (1912).

that some of the assumptions implicit in these calculations are not fulfilled.¹ In the case of potassium chloride the agreement between the several values of the percentage ionization is all that could be desired;² this serves to demonstrate the trustworthiness of the method here described, since the mean difference between these new observations and the weighted mean—in this case of a large number of (somewhat discordant) results published by eleven different authors—is no greater than 0.0001° (or the corresponding amount in terms of concentration).

It is thus evident that by the proper choice of method and apparatus it is possible to determine freezing-point depressions with an accuracy of 0.0001° . Indeed there appears to be no inherent reason why it should not be practicable to attain a tenfold accuracy by the use of a still more sensitive differential temperature measuring device, and of a still more refined means of determining the concentration of the equilibrium solution, both of which appear from our experience to be within the limits of practicability.

Summary.

Trustworthy values of the mol-number and of the corresponding ionization value can be derived from observations of the depression of freezing point only when the concentration, as well as the temperature, of the solution in equilibrium with ice have been determined with sufficient, and commensurate, accuracy. In the work described in the preceding pages the depression was measured directly with an uncertainty of not more than 0.0001° by means of a 50-junction copper-constantan differential thermoelement (which gives 2000 microvolts per degree) and a potentiometric system which enabled the electromotive force to be read to 0.1 microvolt. A prerequisite for the attainment of this degree of accuracy is a condition of stationary equilibrium, which was secured by thorough mixing of the solution with a large quantity of ice in a vacuum-jacketed vessel completely surrounded by melting ice. The concentration of the equilibrium solution was determined by a zero method in which a Zeiss interferometer was used as a means of comparison; the sensitiveness of this method is about 2 parts of solute per million of water.

Results are presented for solutions of the non-electrolyte mannite and of the salts potassium nitrate and chloride at concentrations ranging from 0.004 to 0.1 formula weights per 1000 g. water; consideration of these shows that the method is susceptible of the accuracy claimed for it.

WASHINGTON, D. C.

¹ Cf. Noyes and Falk, *Ibid.*, 34, 488 (1912).

² Kraus and Bray (*THIS JOURNAL*, 35, 1412 (1913)) conclude that the value of Λ_0 for KCl is 128.3 at 18° ; on this basis the ionization values given in Col. V of Table IV should be increased in the ratio 130/128.3 and the agreement with Col. IV would then be less satisfactory.

ANHYDROUS HYDRAZINE. II. ELECTROLYSIS OF A SOLUTION OF SODIUM HYDRAZIDE IN ANHYDROUS HYDRAZINE.¹

By T. W. B. WILSH.

Received January 11, 1915.

The hydrides of the elements in the second series, Groups V, VI, and VII of the Mendeléeff periodic table have, in so far as they have been studied from this point of view, been found; (1) to be very poor conductors of the electric current; (2) to act as solvents for certain inorganic salts; and (3) to behave as ionizing solvents. Ammonia, for example, has been extensively studied by Gore,² Cady,³ Goodwin and Thompson,⁴ Frenzel,⁵ Franklin and Kraus,⁶ and Franklin.⁷

Ostwald,⁸ Hantzsch,⁹ and West¹⁰ have determined the conductivity of aqueous solutions of hydronitric acid. The action of the electric current upon ammonium trinitride in aqueous solution has been investigated by Hittorf.¹¹ Solutions of hydronitric acid and of sodium trinitride have been electrolyzed by Peratoner and Oddo¹² and by Sarvasy.¹³ In 1909 Browne and Lundell¹⁴ electrolyzed solutions of potassium trinitride in anhydrous hydronitric acid and have shown that, while the anhydrous acid is a very poor conductor of the electric current,¹⁵ the solutions of potassium trinitride conduct the current very well indeed.

Calvert¹⁶ found the specific conductivity of hydrogen peroxide to approach that of water. Franklin¹⁷ has shown that hydrogen fluoride possesses strong solvent powers.

Cohen and de Bruyn¹⁸ have shown that anhydrous hydrazine is a poor conductor of the electric current. De Bruyn¹⁹ has determined the solu-

¹ For the first article of this series see Hale and Shetterly, *THIS JOURNAL*, **33**, 1071-6 (1911). The experimental work in this article was completed in January, 1912.

² *Proc. Roy. Soc. London*, **20**, 441 (1872); **21**, 140 (1873).

³ *J. Phys. Chem.*, **1**, 707-13 (1896).

⁴ *Physic. Rev.*, **8**, 38 (1899).

⁵ *Z. Elektrochem.*, **6**, 477-80, 485-9, 492-500 (1900).

⁶ *Am. Chem. J.*, **20**, 820-36 (1898); **23**, 277-313 (1900); **24**, 83 (1900); *THIS JOURNAL*, **27**, 191-222 (1905).

⁷ *Z. physik. Chem.*, **69**, 279 (1909); *Am. Chem. J.*, **47**, 285-317 (1912).

⁸ See Curtius and Rodenhausen, *J. prakt. Chem.*, [2] **43**, 207 (1891).

⁹ *Ber.*, **32**, 3066 (1899).

¹⁰ *J. Chem. Soc.*, **77**, 705 (1900).

¹¹ *Z. physik. Chem.*, **10**, 593 (1892).

¹² *Gazz. chim. ital.*, **25**, II, 13 (1895); *Chem. Zentr.*, **1895**, II, 864.

¹³ *J. Chem. Soc.*, **77**, 603 (1900).

¹⁴ *THIS JOURNAL*, **31**, 435-48 (1909).

¹⁵ This fact has been corroborated in this laboratory by further work that has not yet been published on the conductivity of anhydrous hydronitric acid.

¹⁶ *Drude's Ann. Physik.*, **1**, 483 (1900).

¹⁷ See foot-note, *THIS JOURNAL*, **27**, 821 (1905).

¹⁸ *Proc. Acad. Wetenschappen*, **5**, 551-6 (1903); *J. Chem. Soc.*, **84**, II, 405 (1903).

¹⁹ *Rec. trav. chim.*, **15**, 174-84 (1896).

bilities of sodium chloride, sodium nitrate, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, and barium nitrate in anhydrous hydrazine at 12.5°.

The present paper contains the record of a series of experiments made upon the action of the electric current upon solutions of the hydrazo-base,¹ sodium hydrazide in anhydrous hydrazine. The results obtained have been described under the following headings: (1) preparation of sodium hydrazide, (a) preparation of anhydrous hydrazine, (b) action of anhydrous hydrazine upon sodium amide, (c) action of anhydrous hydrazine upon metallic sodium; (2) apparatus employed in the electrolysis; (3) general procedure; (4) details of experiments; (5) discussion of results; and (6) summary.

Preparation of Sodium Hydrazide.

Lobry de Bruyn² subjected metallic sodium to the action of hydrazine hydrate and anhydrous hydrazine, respectively, and obtained in the first case, a substance to which he assigned the formula N_2H_5ONa , and in the second, the mono-sodium hydrazide. No analyses are given for either product, although it is stated that hydrogen and ammonia are evolved. Later Scandola³ treated finely divided sodium, suspended in ether, with hydrazine hydrate and obtained a white explosive substance, soluble in alcohol and water, but insoluble in ether, petroleum ether and benzene; it decomposes at 58° and is combustible at higher temperatures when heated. No analyses were given. The conclusion was drawn that the substance is different from that obtained by de Bruyn⁴ and may possibly have the formula $HN-NNa$ or $NaN-NNa$.



Ebler and Schott⁵ studied the action of hydrazine hydrate on zinc and found that in absence of air there was no action. In presence of air, however, the hydrazinated zinc salt of hydrazine carboxylic acid, $Zn(O.CO.NH.NH_2)_2.2N_2H_4$ was obtained and analyzed. In 1910 Ebler and Krause⁶ prepared zinc hydrazide, to which they assigned the formula $Zn \begin{array}{c} \diagup N-H \\ | \\ \diagdown N-H \end{array}$ or $Zn:N.NH_2$, by the action of zinc ethyl or zinc diamide on

¹ The term *hydrazo-base* for a metallic hydrazide and *hydrazo-acid* for an acid hydrazide are here suggested in order to follow the nomenclature used by Franklin in connection with the ammonia series of acids, bases, and salts. The behavior of the hydrazine series of acids, bases, and salts in anhydrous hydrazine is now under investigation in this laboratory and will be made the subject of a future communication.

² *Rec. trav. chim.*, 14, 85-88 (1895); 15, 174 (1896).

³ *Estr. Boll. soc. med. Pavia*, 1910; *Chem. Zentr.*, 1910, II, 544.

⁴ *Loc. cit.*

⁵ *J. prakt. Chem.*, [2] 79, 72 (1909).

⁶ *Ber.*, 43, 1690-5 (1910).

hydrazine in anhydrous ether. They suggest that they may possibly have obtained small amounts of $\text{Zn}(\text{NH.NH}_2)_2$ also. The investigators suggest these methods as generally applicable for the preparation of metallic hydrazides.

While preparing anhydrous hydrazine by treating hydrazine hydrate with sodium amide Stollé¹ found that when the sodium amide was present in excess he obtained sodium hydrazide in accordance with the equation²

$$\text{N}_2\text{H}_4 + \text{NaNH}_2 = \text{NaN}_2\text{H}_3 + \text{NH}_3.$$

Preparation of Anhydrous Hydrazine.—The anhydrous hydrazine employed in the experimental work described in this paper was prepared by dehydrating hydrazine hydrate with barium oxide according to the method of de Bruyn³ and using the very convenient apparatus described by Hale and Shetterly.⁴ The apparatus was modified, however, to the extent of having the Vigreux distilling tube jacketed and cooled by running water so as to insure a most efficient condensation during the period of reflux.

Partially dehydrated hydrazine hydrate was boiled in this apparatus for about three hours with about a 50% excess of barium oxide. The water was then removed from the Vigreux condenser, and the hydrazine was distilled under reduced pressure, in an atmosphere of hydrogen, into the container. The product was found by analysis to contain 99.7% hydrazine.

The method used for the determination of hydrazine throughout the present research was that suggested by Rimini⁵ and modified by Hale and Redfield.⁶ Methylene blue was used as indicator in all of the iodine titrations. The hydrazine was kept in small glass-stoppered bottles, the stoppers of which were lubricated with a little of the anhydrous substance. By covering the stoppers and the necks of the bottles with tin foil and holding this tightly in place with rubber bands, circulation of air around the stopper was prevented and the amount of moisture working its way into the anhydrous hydrazine was reduced to a minimum.

Action of Anhydrous Hydrazine upon Sodium Amide.—The sodium amide used was obtained through the courtesy of the Synflour Scientific Laboratories. On analysis it was found to be satisfactory for use in this piece of investigation.

As the result of preliminary experiments performed in this laboratory in 1909 by Dr. C. F. Hale it was found that a very explosive yellow compound was obtained by treatment of sodium amide with 96% hydrazine.

¹ *J. prakt. Chem.*, [2] 83, 200 (1911).

² See Ebler and Krause, and Scandola, *loc. cit.*

³ *Loc. cit.*

⁴ *THIS JOURNAL*, 33, 1071-76 (1911).

⁵ *Gazz. chim. ital.*, 29, I, 265-69 (1899); *Atti accad. Lincei*, [5] 15, II, 320; *Chem. Zentr.*, 1906, II, 1662.

⁶ *THIS JOURNAL*, 33, 1353-62 (1911).

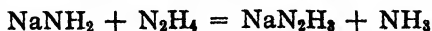
The reaction was conducted in an atmosphere of hydrogen and nitrogen, respectively. In every case the product exploded before it could be analyzed. In one instance, under reduced pressure, a somewhat bluish deposit, probably of metallic sodium, was formed upon the walls of the tube as a result of the explosion.

Experiments were first performed in order to determine the amount of ammonia liberated by the action of a weighed amount of sodium amide on an excess of anhydrous hydrazine. The apparatus employed was a glass-stoppered U-tube of special construction so arranged that the sodium amide and hydrazine could be brought into contact in an atmosphere of hydrogen (purified by bubbling through alkaline pyrogallol and sulfuric acid) and the liberated ammonia driven over and absorbed in sulfuric acid. Any hydrazine that may have been carried over into the absorbing liquid was oxidized by boiling with potassium iodate. The ammonia was determined by making the solution alkaline and distilling into an excess of standard acid.

It was found necessary to use the sodium amide in finely divided form, as otherwise it will react but slowly with the hydrazine on account of a protective coating of the sodium hydrazide which forms on the surface. Action began as soon as the materials were brought into contact with each other. Gas was given off, the powder became yellow, increased in bulk and eventually went into solution in the hydrazine. If the amount of hydrazine was not too great the solution was of an amber-yellow color. If, however, the hydrazine was present in excess of a certain amount, the solution became colorless. On standing, the yellow solution in general became colorless—in a few minutes in case a large excess of hydrazine was present, but only after a long time, several months in some cases, when a small excess was present.

In the three experiments performed 0.0571, 0.0484, and 0.0482 g. of sodium amide were treated, respectively, with a relatively large excess (about 8 cc.) of hydrazine. In the first two experiments, in which the reaction was conducted in an atmosphere of hydrogen, 0.0914 and 0.1024 g. of ammonia were obtained. By far the greater part of this ammonia was liberated during the first violent stage of the reaction. In the third experiment, in which the reaction took place in an atmosphere of pure dry ammonia and in which the evolved gases were collected in a Schiff nitrometer filled with dilute sulfuric acid, 20.8 cc. of nitrogen and 16.3 cc. of hydrogen were obtained.

From these experiments it is apparent that treatment of sodium amide with hydrazine results in the liberation of ammonia, nitrogen, and hydrogen. Since the amount of ammonia formed is far greater than that obtainable from the sodium amide it is possible that the initial hydrazinolysis of the sodium amide in accordance with the equation



is followed by decomposition of a part of the excess of hydrazine with formation of ammonia, nitrogen, and hydrogen. This may be attributable

to a secondary reaction between sodium hydrazide and hydrazine or to a catalytic decomposition such as that suggested by Tanatar.¹

Action of Anhydrous Hydrazine on Metallic Sodium.—The action of anhydrous hydrazine on metallic sodium was studied in a preliminary way in a form of apparatus similar to that described by Browne and Houlehan² and used by them in studying the action of ammonium trinitride in liquid ammonia on certain metals. Small amounts of anhydrous hydrazine and sodium were brought together in approximately equivalent amounts. The hydrazine was weighed out in a Lunge-Rey weighing pipet and was introduced into the U-tube, which was immediately placed in a freezing mixture to freeze the hydrazine and prevent loss by fuming. The proper amount of sodium was then introduced into the pocket. The stopcocks were securely set in position and the U-tube was connected in the usual way with the Schiff nitrometer, filled with dilute sulfuric acid. A current of dry ammonia was now passed through the apparatus until the air was completely displaced, as indicated by the absence of bubbles of unabsorbable gas from the nitrometer. The freezing mixture was now removed and when the hydrazine had melted the sodium was brought into contact with it by jarring the apparatus slightly. The surface of the metal immediately became bright blue and soon after green in color. Gas was evolved and a yellow solid began to form and within a few minutes the whole mass assumed a light yellow color. A moment later and with scarcely any preliminary warning the material in one of the U-tubes exploded, completely wrecking the apparatus. Shortly afterward the other apparatus was destroyed by a similar explosion. Not enough gas was obtained in either case to warrant analysis with the apparatus at hand.

The experiment was repeated in a modified manner so as to eliminate the possibility of an explosion. The same kind of apparatus was employed, but a large excess of hydrazine was used and, as soon as there was evidence of the formation of the yellow solid, ammonia was condensed on the reacting mass by means of solid carbon dioxide and alcohol. The mass then became blue, owing to the solution of sodium in ammonia. The freezing mixture was removed and, as soon as the tube warmed up and the ammonia evaporated, the mass became white and shortly afterward regained the yellow color. Ammonia was again condensed on the mass and again allowed to evaporate. This operation was repeated three times, and the reacting mixture was allowed to stand for about three weeks. At the end of this time the current of ammonia was again turned on in order to carry over any gas that might have collected in the U-tube. The gas was no sooner turned on, however, than the U-tube was completely

¹ *Z. physik. Chem.*, **40**, 475-80 (1902); **41**, 37-42 (1902); see also Purgotti and Zanichelli, *Gazz. chim. ital.*, **34**, 1, 57-87 (1904).

² *THIS JOURNAL*, **33**, 1742-52 (1911).

demolished by a terrific explosion. Analysis of the gas collected in the nitrometer gave 0.2 cc. of hydrogen and 19.3 cc. of nitrogen. Further experiments carried out under somewhat different conditions confirmed the observation that both hydrogen and nitrogen, the former in relatively small amounts, were liberated during the reaction between sodium and hydrazine in the presence of ammonia. It is probable that interaction between the sodium and hydrazine first takes place with formation of sodium hydrazide and liberation of nascent hydrogen in accordance with the equation



That hydrogen is not evolved as gas, except in relatively small amounts, is probably to be explained by the reducing action on hydrazine. The presence of a large proportion of nitrogen in the evolved gases may be attributed either to the liberation of this gas as the result of some secondary reaction that occurs during the reduction of hydrazine, or to the catalytic decomposition of hydrazine; in the author's opinion, however, it is probably due to the ammonolysis of sodium hydrazide with formation of sodium amide, ammonia, and nitrogen. This reaction would be analogous to the hydrolysis of sodium peroxide with formation of sodium hydroxide and oxygen.

The extremely explosive character of the products obtained by the interaction of hydrazine with sodium amide and sodium was found to preclude the possibility of obtaining exact analytical data concerning their composition, without the use of unusual methods. Some evidence has been obtained of the existence not only of the primary sodium hydrazide, NaN_2H_3 , but also of the secondary sodium hydrazide, $\text{Na}_2\text{N}_2\text{H}_2$. Until further work has been done, however, no more definite statement can be made concerning these substances.

Apparatus Employed in the Electrolysis.

Because of the corrosive action of hydrazine upon rubber or cork it was necessary to construct the apparatus used in the electrolysis entirely of glass. Since the oxygen of the air acts on hydrazine it was also necessary that provision should be made to carry on the electrolysis in an atmosphere of some inert gas and yet prevent this gas from contaminating the resulting gaseous products. The apparatus employed is shown in Fig. 1. It consisted of cell A containing the inner tubes B and B' reaching nearly to the bottoms of the two arms. In these inner tubes the two platinum electrodes C and C' were suspended by platinum wires as shown in the figure. The inner tubes B and B' communicated, by means of capillary tubes and the two-way stopcocks D and D' either with the air or through the four-way stopcocks F and F', with the Hempel burets E and E' filled with mercury. Each arm of the cell A could be connected, through the

two-way stopcocks G and G', either with a suction pump or with a source of pure dry nitrogen. The capillary stopcocks H and H', respectively, permitted the introduction of the electrolyte from the graduated glass-stoppered mixing tube K, and the drawing off of samples at the con-

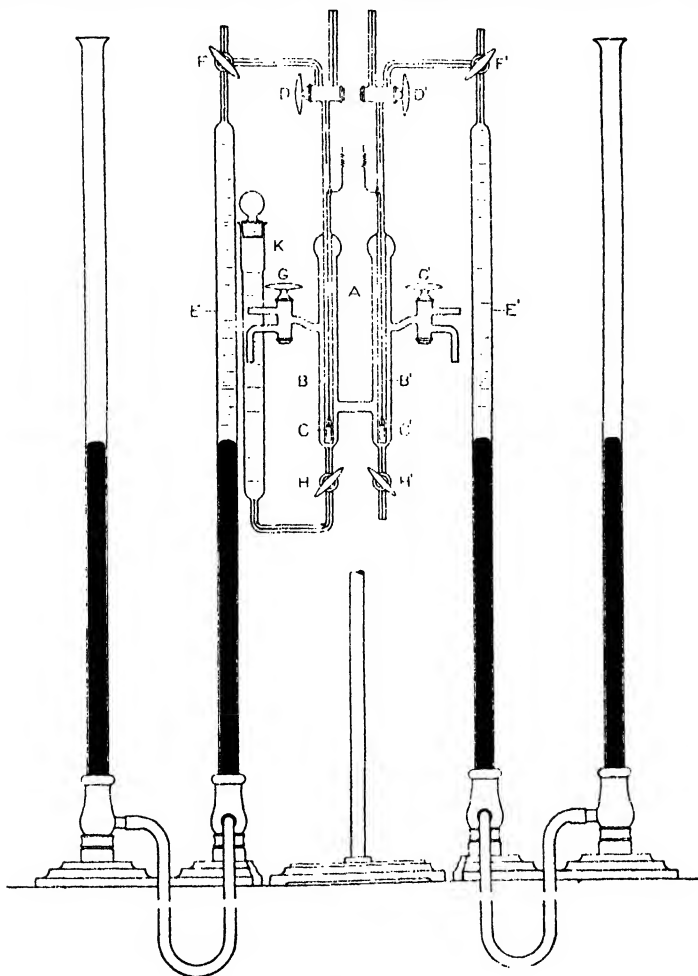


Fig. 1.

clusion of the experiment. The whole apparatus was supported by suitable clamps and, with the exception of the two leveling tubes, was rigidly mounted upon a wooden base. The stopcocks, lubricated with a small amount of anhydrous hydrazine, were securely wired in place.

General Procedure.

The cell was thoroughly cleaned and dried, and the air was displaced by dry nitrogen. The proper amount of anhydrous hydrazine was then

introduced into K and a slow stream of nitrogen allowed to bubble through it by opening either G or G' and properly adjusting H. The nitrogen was allowed to escape from K around the glass stopper, which was kept from fitting tightly by means of a fine platinum wire. In the experiments in which sodium amide was used a weighed amount of this substance was introduced directly into the hydrazine. When metallic sodium was employed, ordinary glass tubing was drawn out to small diameter and cut into approximately 10 mm. lengths. These were weighed, molten sodium was drawn up into them, and they were again weighed. A tube was then placed on a flat surface, crushed by means of a pestle and the resulting sodium wire with the crushed glass adhering was then quickly introduced into the hydrazine in the mixing tube. This operation was repeated until sufficient sodium was in solution. This gave a means of employing small amounts of sodium with a clean surface while the adhering particles of glass prevented too violent a reaction. When sodium amide is used it must be introduced a little at a time, otherwise frothing will result and the stopper will be forced out, with consequent loss of hydrazine. The nitrogen which was kept bubbling through the liquid served to prevent the oxidation at the surface and also stirred the liquid, giving a homogeneous solution.

The stopcock H was now closed, the cell was partially evacuated, H was opened and the solution was slowly sucked over into A. While passing from the mixing tube into the cell the solution was filtered through glass wool, which had previously been placed in the bottom of the mixing tube. When sufficient solution had been introduced into the cell, H was closed, D and D' were opened to the air, and nitrogen was admitted at G or G' under pressure sufficient to force the solution up into B and B' until they were completely filled. D and D' were then closed, the supply of nitrogen was shut off and G and G' were opened to the air a moment to allow the pressures and the levels of the columns of liquid in the cell arms to equalize themselves. A millimeter and a copper coulometer were connected in series with the cell and a voltmeter was shunted across the cell terminals. The voltmeter was in circuit for a few seconds only at the time of each reading, so that the total amount of current passing through it was negligible in any one experiment. During an experiment the gaseous products of the electrolysis that accumulated in B and B' were from time to time drawn over into the burets by proper manipulation of the stopcocks D, D', F, and F'. The gases were analyzed by transferring them from E and E' to a water-jacketed Hempel buret containing mercury, on the surface of which were a few millimeters of water. Any hydrazine vapor or ammonia was removed by absorption in a pipet containing dilute sulfuric acid. In order to detect possible leakage of air into the apparatus, oxygen was determined by absorption in alkaline pyrogallol. Hydrogen was

determined with palladium black and the nitrogen was obtained by difference. The palladium tube was filled with nitrogen each time before use which obviated the necessity of correcting for the contraction due to the presence of oxygen.

Details of Experiments.

Experiment 1.—After electrolysis for about five hours the solution, which was colorless at the outset, became yellow in the neighborhood of the cathode. The circuit was now broken and the solutions in the two arms of the cell were thoroughly mixed, with the result that the yellow color disappeared. After three hours of further electrolysis the cathode solution again became yellow and it was allowed to remain so until the end of the experiment. A small amount of a yellowish solid seemed to be deposited on the cathode. During the electrolysis, the total duration of which was eleven hours and thirty-five minutes, the current dropped from 9.5 to 2.9 milliamperes and the voltage rose from 89 to 107 volts.

Experiment 2.—In order to ascertain whether the yellow color that appeared in the cathode tube during the preceding experiment could be transferred to the opposite side of the cell, the solution obtained during the previous experiment was subjected to further electrolysis for a period of twelve hours with the direction of the current reversed. The yellow solution which was now in the anode tube gradually became colorless while the colorless solution in the cathode tube assumed the usual yellow color. During this experiment which was essentially a continuation of Expt. 1 the current fell from 3 to 1.2 milliamperes and the voltage increased from 90 to 102 volts.

Experiment 3.—The solution in this experiment was the same as that used in Expt. 2. It was thoroughly stirred at the outset, however, by means of the current of nitrogen. During the adjustment of the level of the mercury in the buret connected with the cathode tube, a few drops of mercury accidentally passed over through the inner tube and came into contact with the electrode, spreading over the whole surface in a peculiar manner. The electrolysis was, therefore, conducted virtually with a mercury cathode. The usual evolution of gas at the cathode did not take place. The surface of the mercury soon darkened, became purple, and was finally covered with a mass of purplish needle-like crystals which showed a brownish color at the lower end of the electrode. If this material was a sodium amalgam it gave no evidence of any chemical action even after the electrolysis had been discontinued, but stood in contact with the electrolyte apparently unchanged for several days. Gas was evolved as usual from the anode throughout the experiment which covered a period of about nine hours. The usual yellow color appeared in the neighborhood of the cathode. Toward the middle of the experiment the current dropped from 4 to 1 milliamperes and from 102 to 92 volts.

Experiment 4.—The electrolyte employed in the previous experiment was thoroughly stirred, without, however, disturbing the crystals on the cathode. The direction of the current was now reversed thus making the electrode holding the purplish crystals the anode and the clean platinum electrode the cathode. At the beginning of the experiment no gas was evolved at the anode but the crystals underwent a gradual disintegration and in a short time gave place to liquid mercury which adhered to the electrode. As soon as this transformation was complete gas was evolved at the anode while the mercury soon became tarnished to a brassy yellow color which faded out gradually when the circuit was broken and left the mercury surface bright and clean. The solution in the neighborhood of the cathode became yellow as before. The gases were not analyzed.

Experiment 5.—After the conclusion of Expt. 4 the electrolyte was thoroughly stirred until it became colorless. The mercury electrode was made the anode. As

soon as the electrolysis started the clean mercury surface became tarnished as in Expt. 4. The solution in the cathode tube became yellow. The current varied from 4.8 to 1.7 milliamperes and the voltage increased from 100 to 102 volts during the progress of the experiment.

Experiment 6.—The contents of the cell were removed and the cell and electrodes were thoroughly cleaned and dried. The electrolyte used had, at the outset, a deep yellow color. The duration of the electrolysis was six hours and twenty-two minutes. At the end of the first half-hour the solution in the inner anode tube had become colorless. An hour later the whole solution in the anode compartment had lost its yellow color while that in the cathode compartment became deep yellow in color. The current dropped from 5.6 to 3.1 milliamperes and the voltage increased from 99 to 105 volts during the experiment.

Experiment 7.—The electrolyte used in the preceding experiment was thoroughly stirred, with the result that it became entirely colorless. A few drops of mercury were introduced into the anode compartment so as to coat the electrode as in Expt. 3. As before, no evolution of gas was observed at the cathode during the electrolysis, but a crystalline solid similar in appearance to that previously obtained was deposited on the electrode. At the conclusion of the experiment, which lasted for ten hours and twenty-two minutes, the solution in the cathode tube had become very yellow in color. The current fell from 3.1 to 1.1 milliamperes and from 105 to 101 volts during the course of the experiment.

Experiment 8.—The mercury remaining on the electrode from the preceding experiment was removed with nitric acid, leaving the platinum clean and bright, and the cell was thoroughly cleaned and dried. The new solution employed in this case was intensely yellow and showed a much lower resistance than the electrolytes previously used. The electrolysis was continued for one hour, during which period a vigorous evolution of gas was observed at both electrodes. A blue deposit, probably consisting of either metallic sodium or an addition product of sodium with hydrazine, was at once formed on the cathode. This remained only for a short time, however, after the circuit was broken, quickly dissolving in the electrolyte with evolution of gas. Throughout the entire cell the solution remained yellow during the experiment. The current dropped from 115 to 105 milliamperes and from 85 to 80 volts.

Experiment 9.—During the preparation of the electrolyte used in this experiment a yellow solid was at first formed, which subsequently dissolved yielding a dark yellow solution. In the course of the electrolysis, which was continued for a period of one and one-half hours, a slight blue deposit was formed on the cathode. Small portions of this deposit appeared to be continuously projected from the surface of the cathode, subsequently dissolving with appreciable evolution of gas. The whole solution remained yellow, and at the end of the experiment a very slight deposit of a dull black color remained on the cathode. This deposit seemed to dissolve very slowly in the electrolyte with evolution of small amounts of gas. The current increased from 50 to 58 milliamperes while the voltage remained practically constant at 38 volts.

Experiment 10.—The electrolyte used in Expt. 9 was thoroughly stirred and was subjected to further electrolysis for a period of thirteen and one-half hours. In this case the blue deposit was not formed on the cathode but the black substance appeared as before. After the circuit was broken this material gradually disappeared with slow evolution of gas. The whole solution remained yellow throughout the experiment. The current was held practically constant at 7 milliamperes and 5.5 volts.

Experiment 11.—The solution used in the last two experiments was again electrolyzed, after it had been thoroughly stirred, for a period of fourteen hours and thirty-five minutes. The current was held practically constant at 8.5 milliamperes and 6 volts. Similar phenomena to those described under Expt. 10 were noted.

Experiment 12.—The same solution was thoroughly stirred and was electrolyzed for two hours and five minutes. Although the current density was somewhat higher than in Expt. 11 the same phenomena were noted and no blue deposit was formed. The current was nearly constant at 25 milliamperes and at 16 volts.

Experiment 13.—The conditions prevailing in Expt. 12 were duplicated as nearly as possible. The phenomena noted were similar in every particular to those described under the preceding experiments. The current averaged 24 milliamperes and 17 volts.

Further details of the experiments are summarized in Table I.

TABLE I.—RESULTS OBTAINED IN ELECTROLYTIC EXPERIMENTS.

| Number of Expt. | NaNH ₂ or Na used. Grams. | N ₂ H ₄ used. Cc. | Copper on coulometer cathode. | Gas evolved at anode. | | Ratio Cu : N (anode). | Gas evolved at cathode. | |
|-----------------|--------------------------------------|---|-------------------------------|-----------------------|---------------|-----------------------|-------------------------|---------------|
| | | | | Nitrogen. Cc. | Hydrogen. Cc. | | Nitrogen. Cc. | Hydrogen. Cc. |
| 1 | NaNH ₂ 0.3 | 40 | 0.0605 g. | 16.2 | 0.7 | 1 : 1.5 | 2.6 | 2.4 |
| 2 | NaNH ₂ 0.3 | 40 | 0.0950 g. | 20.0 | 2.2 | 1 : 1.2 | 14.4 | 13.1 |
| 3 | NaNH ₂ 0.3 | 40 | 0.024 † g. | 4.8 | 0.0 | 1 : 1.1 | | |
| 4 | NaNH ₂ 0.3 | 40 | | | | | | |
| 5 | NaNH ₂ 0.3 | 40 | 0.0232 g. | 4.6 | 0.8 | 1 : 1.3 | | |
| 6 | Na 0.1 | 40 | 0.0304 g. | 5.9 | 0.5 | 1 : 1.1 | 1.1 | 5.4 |
| 7 | Na 0.1 | 40 | 0.0201 g. | 4.6 | 0.4 | 1 : 1.2 | | |
| 8 | Na 0.5 | 35 | 0.0890 g. | 23.3 | 14.2 | 1 : 1.5 | 8.3 | 12.6 |
| 9 | Na 1.0 | 33 | 0.0999 g. | 39.2 | 4.3 | 1 : 2.2 | 7.3 | 7.4 |
| 10 | Na 1.0 | 33 | 0.1004 g. | 36.6 | 6.2 | 1 : 2.1 | 13.1 | 23.8 |
| 11 | Na 1.0 | 33 | 0.1291 g. | 56.9 | 10.8 | 1 : 2.5 | 2.4 | 32.0 |
| 12 | Na 1.0 | 33 | 0.0592 g. | 27.2 | 4.4 | 1 : 2.6 | 1.9 | 13.8 |
| 13 | Na 1.0 | 33 | 0.0665 g. | 30.9 | 2.9 | 1 : 2.6 | 2.4 | 15.5 |

Discussion of Results.

Among the numerous ionic species that might be assumed to be present in a solution of sodium hydrazide in anhydrous hydrazine are Na⁺, N₂H₃⁻, N₂H₂⁼, N₂H⁼, and N₂⁼. That Na⁺ is present as ion is indicated by the appearance of the blue cathode deposit noted in several experiments. This indication is further confirmed by the results obtained during the electrolysis of the solutions with a mercury cathode.

The sodium liberated would, of course, act upon the solvent with formation of sodium hydrazide and evolution of hydrogen, at least part of which reacts with hydrazine to form ammonia. On the basis of this explanation it is not surprising to find that the volume of hydrogen liberated at the cathode is distinctly lower than that required for the theoretical ratio Cu : 2H. The liberation of nitrogen at the cathode may be explained as a result of the action of sodium upon hydrazine as already described in connection with the preliminary study of this reaction, that is, as a result of ammonolysis of the sodium hydrazide.

It seems reasonable to suppose that the principal anion present in the electrolyte is N₂H₃⁻. This ion in anhydrous hydrazine would be analogous to the OH⁻ ion in water and to the NH₂⁻ ion in liquid ammonia. Assuming for the present that no condensation products are formed at the anode it is probable that four N₂H₃⁻ ions would react with liberation of one molecule

of nitrogen gas and regeneration of three molecules of hydrazine, or it may be that the N_2H_3^- ions discharge upon hydrazine molecules with formation of $\text{N}_2\text{H}_2^=$, or $\text{N}_2\text{H}^{\equiv}$ ions which then react yielding as before nitrogen gas and hydrazine. Any of these three sorts of ions might still further be considered to discharge upon hydrazine yielding the ion N_2^{--} which, finally discharging on the anode, would be directly converted into nitrogen gas. In any event one atom of nitrogen would be liberated at the anode for each atom of copper deposited on the coulometer cathode.

This theoretical ratio Cu : N is approximately realized in the first eight experiments in which the concentration of the electrolyte with respect to sodium hydrazide is relatively low. The excess of nitrogen found as well as the presence of hydrogen is probably to be accounted for either by the failure of the regeneration of hydrazine to take place quantitatively or by the slight catalytic decomposition of the solvent.

In Expts. 9 to 13, inclusive, in which the concentration was distinctly higher, the ratio of copper to nitrogen was much lower, averaging 1 : 2.4. This points to more extensive decomposition either of the discharged anions or of the solvent under these conditions.

Summary.

In the present investigation it has been shown that:

(1) Sodium derivatives of hydrazine may be prepared by the action of anhydrous hydrazine upon either metallic sodium or sodium amide.

(2) Solutions of sodium hydrazide in anhydrous hydrazine readily conduct the current, yielding in general nitrogen and hydrogen at both anode and cathode. For each gram atom of copper deposited on the coulometer cathode from 1.1 to 1.5 g. atoms of nitrogen gas were liberated at the anode when the electrolyte was rather dilute. With a more highly concentrated solution, however, the ratio Cu : N varied from 1 : 2.1 to 1 : 2.6.

This investigation was undertaken at the suggestion of Professor A. W. Browne and was carried out with his coöperation.

CORNELL UNIVERSITY,
ITHACA, N. Y.

[CONTRIBUTION FROM DEPARTMENT OF PHYSICAL CHEMISTRY, CHEMICAL LABORATORIES
OF THE UNIVERSITY OF MARBURG.]

THE SOLUBILITY OF CERTAIN DIFFICULTLY SOLUBLE SILVER SALTS.

By A. THIEL.

Received July 1, 1914.

In an article of the above title in *THIS JOURNAL*, 30, 68 (1908), which has only recently come to my attention, A. E. Hill describes several determinations of the ratio of the solubilities AgCl, AgBr, AgI and AgCNS.

He proceeds by determining the concentration of the respective anions in the solution in equilibrium with two of the salts as solid phases. Upon putting a value for silver chloride obtained in another manner into the equation, he can indirectly determine the solubility of the above-named salts on the basis of the solubility relations found according to his method. The procedure employed by Hill has repeatedly been applied for similar purposes before this and it will give reliable results in all of those cases in which the fundamental assumption is complied with, namely, that the two salts are present in the pure state as the solid phases. Apparently the author has not taken the earlier original literature upon this subject into account sufficiently and, consequently, has overlooked the fact that the necessary assumption which makes the method applicable does not apply in a number of the cases considered. Thus, F. W. Kuester and I have been able to show¹ that AgBr and AgI, as well as AgBr and AgCNS, form solid solutions, and that the solid phases in these cases, provided the concentrations of the two species of anions in the solution do not differ too greatly from one another, consist of the two saturated solid solutions. The measurements of Hill on the systems AgBr + AgI and AgBr + AgCNS do therefore in no case give the ratio of the solubilities of the pure salts, but that of the partial solubilities of these salts from the solid phase present. As one can conclude from the tables given in the case of the bromide-iodide mixture, this solid phase consisted partly of the two saturated solutions and also of an unsaturated solid phase; in the case of the bromide-thiocyanate mixture it always consisted of the two saturated solid solutions (AgBr in AgCNS and *vice versa*).

As far as the silver iodide is concerned the effect produced upon the calculated solubility is not great, since the silver bromide which is dissolved in the silver iodide does not affect the solubility of the latter in water very greatly. When fresh portions of silver bromide are added one probably obtains a false equilibrium of great inactivity, the position of which does not vary much from that of the unstable system $\text{AgBr}_{\text{pure}} + \text{AgI}_{\text{pure}}$. On the other hand, the influence of an admixture of the second component on the solubility of a solid phase is very great in the system AgBr + AgCNS, and if the results obtained by Hill nevertheless agree well with those obtained by other methods the agreement is to be considered accidental.

If the system AgCl + AgBr had been examined in the same manner, in which case an uninterrupted series of solid solutions is formed, a striking inconsistency of the solubility relations would have at once been apparent, showing the method to be inapplicable.

Among the influences responsible for the accidental agreement of the values of Hill, one might, perhaps, assume the fact that the author has

¹ *Z. anorg. Chem.*, **19**, 81 (1899); **24**, 1 (1900); **33**, 129 (1902).

taken as the standard for the solubility of silver chloride an old result of Kohlrausch and Rose and further does not make use of the more recent values,¹ known at the time, for comparison with the other solubilities calculated by him. If this is done, conditions are not changed markedly. The evidence of solubility determinations, according to a method based upon assumptions insufficiently complied with, is not to be valued too highly in the cases under discussion. Yet one may draw the conclusion from the results obtained in the system $\text{AgBr} + \text{AgCNS}$, that the partial solubilities of the two components, as compared with the solubilities of the pure substances, are diminished in practically the same ratio. This follows from the fact that the solubilities of the two solid components in one another, in mol percentages, are of the same magnitude.

MARBURG A/L GERMANY.

[CONTRIBUTIONS FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY.]

THE RELATIVE SOLUBILITY OF CERTAIN SILVER SALTS.

By ARTHUR E. HILL.

Received December 24, 1914.

The foregoing paper² by Professor Thiel contains five specific criticisms of my publication on "The Relative Solubility of the Silver Halides and Silver Sulfocyanate."³ They may be stated briefly as follows: (1) the publication criticised shows unfamiliarity with the work of Küster and Thiel,⁴ who have shown that solid solutions exist in the cases of AgBr and AgCNS and of AgBr and AgI ; (2) if equilibrium experiments had been made with the salts AgCl and AgBr , the method would have been found unsuited for solubility calculations; (3) the correct value obtained for the solubility ratio of AgBr and AgCNS is accidental; (4) the correct value obtained for the solubility ratio of AgBr and AgI is due probably to a false equilibrium, and finally, (5) all agreement shown may be due to the use in the calculations of the old value obtained by Kohlrausch and Rose for the solubility of silver chloride, instead of more recent values to which Thiel refers. Brief comment may be made on each of these criticisms.

The first criticism must be accepted as justified. I did not know of Küster and Thiel's work on these solid solutions until after the publication of my paper. In this instance it seems to me fortunate that I was unacquainted with their work at that time, for if I had read the publications I might possibly have been discouraged from using these salts in my research. In that event the equilibrium method might not have been ap-

¹ F. Kohlrausch, *Z. physik. Chem.*, **44**, 197 (1903); **50**, 355 (1908); W. Böttger, *Ibid.*, **46**, 521 (1903).

² THIS JOURNAL.

³ *Ibid.*, **30**, 68 (1908).

⁴ *Z. anorg. Chem.*, **19**, 81 (1899); **24**, 1 (1900); **33**, 129 (1902).

plied in a case where it has actually led to very accurate results, having to do with widely dissimilar solubilities. It should be stated, however, that during the progress of the experiments, the behavior of the precipitated silver bromide and sulfocyanate did suggest the formation of a solid solution, as was specifically noted in the publication;¹ for this reason the limitation of the experiments to certain concentrations was found necessary. It appears, therefore, that the experimental method of attacking this problem led to a correct estimate of the influence which solid solution has upon it, whereas an approach to the question from the theoretical side has led Thiel to an over-estimate of this influence.

The second criticism is founded on an assumption as to errors which might have been committed but were not. It seems to require no answer.

The third criticism is that the correct value for the silver bromide-sulfocyanate ratio is accidental. It is odd to find that the same accident, if Thiel maintains it to be such, has affected the experiments which Thiel has made on the same salts, for it is possible to calculate from Küster and Thiel's experiments² a relative solubility of these two salts in substantial agreement with my own values. One may take from Experiments 4, 5¹, 5², and 5³ of their table on page 133 the mean value 33.1 as the molecular percentage of bromide in solution in equilibrium with silver bromide and sulfocyanate, or with solid solutions of the two, if solid solution is the condition of the solid phases. The graphic representation which they give shows that this value (33.1% bromide in solution to 66.9% sulfocyanate) is very constant, even when the composition of the solid phase varies all the way from about 3% silver bromide to 97% bromide. Throughout this wide range, therefore, the equilibrium solution remains constant in composition. Applying to Küster and Thiel's experiments the same method of calculation used in my publication³ we have

$$\frac{\text{Solubility of AgBr}}{\text{Solubility of AgCNS}} = \frac{\sqrt{\text{Bromide in solution}}}{\sqrt{\text{Sulphocyanate in solution}}} = \frac{\sqrt{33.1}}{\sqrt{66.9}} = 0.703.$$

This value is in very reasonable agreement with the average value found by myself, *viz.*, 0.735. The experiment differs from my own in that the total concentration of soluble salt was about 0.1 *N*, whereas in my experiments the concentrations were 0.2 *N* and 0.05 *N*. A tabular presentation of these values will make clear the substantial agreement.

| | Concentration in solution. | Solubility ratio, $\frac{\text{AgBr}}{\text{AgCNS}}$ |
|-------------------------|-------------------------------|---|
| (Hill)..... | 0.2 <i>N</i> | 0.737 |
| (Küster and Thiel)..... | 0.1 <i>N</i> | 0.703 |
| (Hill)..... | 0.05 <i>N</i> | 0.732 |

¹ THIS JOURNAL, 30, 73 (1908).

² *Z. anorg. Chem.*, 33, 133 (1902).

³ THIS JOURNAL, 30, 68 (1908) (Equation 4).

It appears, therefore, that there is agreement within a few per cent. between Küster and Thiel's experiments, and those criticized. Since these tabulated figures represent four experiments by Küster and Thiel, equilibrium being attained from one direction, and four experiments by myself, equilibrium being attained from both directions, it seems fair, on the basis of the theory of chances, to exclude accident from the list of causes contributing to the agreement of these figures with those obtained by other methods.

It seems equally unnecessary to adopt Thiel's hypothesis of a false equilibrium as responsible for the correct results in the silver bromide-iodide solubility ratio. One can calculate again from Thiel's independent¹ experiments, substantially the same ratio found by myself. Experiments 4, 5 and 6 of Thiel's table suggest the same condition as in the case previously discussed, *i. e.*, while there is a wide variation in the composition of the precipitate, there is substantial constancy in the composition of the solution. This is evidently the solution in equilibrium with the two solids, and its composition is the mean of 0.38, 0.32 and 0.32 parts of iodide to the mean of 997, 998, and 997 of bromide, *i. e.*, 0.34 to 998. From these figures the solubility ratio is calculated as 0.01845, which is again in reasonable agreement with the mean value 0.014 found by myself. This is as close as can be expected, considering that the three figures of Thiel's taken vary by 18%, and that the analytical method used by myself was conceded to have necessarily a large possible error. The ratio of these two solubilities, as given in Thiel's compilation, has been found as follows at the temperature of these experiments (25°):

Thiel, 0.0130 by potential measurements;

Holleman, 0.0115 by conductivity measurements;

Goodwin, 0.0147 by potential measurements.

The value of Holleman, which varies most from the value 0.014 found by me, has been obtained by calculation from measurements made at other temperatures. Since the value 0.014 is between the extremes found by others, and since that value is at least partially sustained by Thiel's own experiments quoted, with a different total concentration of soluble halide present, it seems to be entirely unnecessary to explain it away by an assumption of a false equilibrium.

The final statement, that the apparent agreement may be due to the use of antiquated solubility figures, is less careful than one expects from a critic; the figures in Abegg and Cox's² compilation were used and quoted, thus taking cognizance of all reliable data existent at that time. The additional references which Professor Thiel gives are for other temperatures, and therefore entirely unsuited to the calculations under discussion.

¹ *Z. anorg. Chem.*, 24, 29 (1900).

² *Z. phys. Chem.*, 46, 11 (1903).

If any other of the accepted values for 25° is taken as standard in place of the classical value of Kohlrausch's selected by me, the agreement between my method and the others which have been used will be found to be better than was stated in my earlier publication. This is so obvious on inspection of my table¹ that it seems unnecessary to quote figures.

To Professor Thiel's conclusion with reference to the partial solubilities of silver bromide and sulfocyanate, may be added the conclusion that in these cases solid solution is not a factor of sufficient influence to affect the solubility equilibria noticeably, as proved by the experiments under discussion. The question is also suggested, though its discussion would be out of place in this reply, as to what is really meant by "solid solution" when applied to amorphous bodies such as the salts used by Thiel and myself.

NEW YORK UNIVERSITY, NEW YORK.

[LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

ABSORPTION AND THE SURFACE TENSIONS OF AQUEOUS SOLUTION OF HOMOLOGOUS FATTY ACIDS AND ALCOHOLS.

BY MARKS NEIDLE.

Received December 23, 1914.

Duclaux² was the first to present the following relationship between the concentrations of aqueous solutions of homologous fatty alcohols and acids and their surface tensions; the ratio of the concentrations of any two homologous acids or alcohols which have the same surface tension is a constant, independent of the value of the surface tension. In symbols this may be expressed by the following equation, which will be referred to as the Duclaux equation:

$$c = bf(\gamma), \quad (1)$$

where c is the concentration, $f(\gamma)$ a fixed function of the surface tension for all members of a series, and b a constant depending upon the particular member of the series. The experimental basis for this rule comprised the surface tensions of methyl, ethyl, isopropyl, isoamyl and caprylic alcohols, and formic, acetic and butyric acids, determined by a very crude drop method. The values of the concentration ratios reproduced in Table I show as good agreement as could be expected from such rough data. The concentrations c are expressed in percentages by volume, and the temperature of observations is 15° .

Using the Morgan drop-weight method, Morgan and Neidle³ found the surface tensions of aqueous solutions of methyl, ethyl and amyl alcohols,

¹ *Loc. cit.*, 74.

² *Ann. chim. phys.*, [5] 13, 76 (1878).

³ *THIS JOURNAL*, 35, 1856 (1913).

TABLE I.

| Rel. surf. tens. (Water = 1.) | $\frac{C(\text{Me.OH})}{C(\text{Am.OH})}$ | $\frac{C(\text{Et.OH})}{C(\text{Am.OH})}$ | $\frac{C(\text{Prop.OH})}{C(\text{Am.OH})}$ | $\frac{C(\text{But.OH})}{C(\text{Am.OH})}$ | $\frac{C(\text{Cap.OH})}{C(\text{Am.OH})}$ | $\frac{C(\text{Formic acid})}{C(\text{Acetic acid})}$ | $\frac{C(\text{But. acid})}{C(\text{Acetic acid})}$ |
|----------------------------------|---|---|---|--|--|---|---|
| 0.90 | 33 | 16 | ... | 2.7 | ... | 2.9 | 0.10 |
| 0.85 | 34 | 17 | ... | 2.8 | ... | 3.1 | 0.10 |
| 0.80 | 34 | 18 | 9.1 | 2.8 | 0.057 | 3.0 | 0.11 |
| 0.75 | 33 | 18 | ... | ... | ... | 3.0 | 0.12 |
| 0.70 | 33 | 18 | ... | 2.8 | 0.061 | 2.9 | 0.10 |
| 0.65 | 31 | 17 | ... | 2.6 | ... | 3.0 | 0.10 |
| 0.60 | .. | 18 | 9.3 | 2.6 | 0.063 | ... | 0.10 |
| 0.55 | .. | 18 | ... | 2.6 | ... | ... | |
| 0.50 | .. | 16 | ... | 2.6 | 0.064 | ... | |
| 0.45 | .. | 16 | ... | 2.6 | ... | ... | |
| 0.40 | .. | 16 | 9.3 | 2.6 | ... | ... | |

and of formic and acetic acids. With the results obtained, the Duclaux equation was tested and found to hold very well for dilute solutions as is seen from Table II. The concentrations are expressed in grams per 100 cc., and the temperature of observations is 30°.

TABLE II.

| Surf. tens. Dynes/cm. | $\frac{C(\text{Me.OH})}{C(\text{Et.OH})}$ | $\frac{C(\text{Et.OH})}{C(\text{Am.OH})}$ | Surf. tens. Dynes/cm. | $\frac{C(\text{Formic acid})}{C(\text{Acetic acid})}$ |
|--------------------------|---|---|--------------------------|---|
| 46 | 1.95 | 18.3 | 51 | 3.18 |
| 48 | 1.98 | 18.3 | 55 | 3.13 |
| 50 | 2.01 | 18.9 | 56 | 3.08 |
| 52 | 2.04 | 18.9 | 57 | 3.05 |
| 54 | 2.08 | 18.9 | 59 | 3.05 |
| 56 | 2.10 | 18.9 | 61 | 3.06 |
| 58 | 2.11 | 19.0 | 63 | 3.04 |
| 60 | 2.11 | 19.0 | 64 | 3.05 |
| 62 | 2.13 | 18.9 | 65 | 3.05 |
| 64 | 2.10 | 18.9 | .. | |

The concentration ratios for methyl and ethyl alcohols at concentrations which give surface tensions less than 54 dynes/cm. (Et.OH 4.53, Me.OH 9.50 g./100 cc.) agree within less than 1%. The agreement in the pair ethyl and amyl alcohols is even closer and extends to more concentrated solutions, which is also true for the pair, formic and acetic acids. Since the concentrations having the same surface tensions were found by graphic interpolation, and it is difficult to read low values with a high degree of precision, the ratios between 65 and 71.03 dynes/cm., the surface tension of pure water, were not investigated; but it is evident from the graphs that these would show even greater constancy than those at lower surface tensions. The Duclaux equation is thus established for the three alcohols

and two acids considered above, and it is very probable that it will also be substantiated for the others investigated by Duclaux, when their surface tensions are determined by the Morgan drop-weight method or any other reliable method.

Having found the surface tensions of aqueous solutions of one member of the series for a number of concentrations, the Duclaux equation may be applied to calculate those of aqueous solutions of another homolog within certain limits of concentration. For this purpose we need only determine the surface tension at any one concentration within the same limits. It will be necessary, however, before making this application to new homologs, to extend the experimental basis in order to see how far down the series the relationship holds. Such work is contemplated in this laboratory.

A relationship will now be deduced, connecting adsorption and surface tensions of aqueous solutions of homologous fatty acids and alcohols, which may be considered the physico-chemical interpretation of the Duclaux equation. The adsorption or excess concentration of the solute in the surface of a solution, expressed in mols per square centimeter, is given by the Gibbs adsorption equation

$$\Gamma = - \frac{C}{iRT} \frac{d\gamma}{dc}, \quad (2)$$

where c , the concentration of the solution, may evidently be expressed in grams or mols per 100 cc. or liter, and i is the van't Hoff factor.

From Equation 1 we have

$$\frac{dc}{d\gamma} = bf'(\gamma) \quad \text{and} \quad c \frac{d\gamma}{dc} = \frac{f(\gamma)}{f'(\gamma)}.$$

Substituting in (2), we find

$$\Gamma = - \frac{f(\gamma)}{iRTf'(\gamma)}. \quad (3)$$

But for homologs $f(\gamma)$ and $f'(\gamma)$ are the same, therefore the adsorption of their solutions having the same surface tension and the same temperature is inversely proportional to their van't Hoff factors, *i. e.*,

$$(\Gamma_1/\Gamma_2)_{\gamma,T} = i_2/i_1.$$

In the case of non-electrolytes, this relation becomes simpler, since $i_1 = i_2 = 1$, and consequently

$$(\Gamma_1)_{\gamma,T} = (\Gamma_2)_{\gamma,T}.$$

Hence in dilute aqueous solutions of the fatty acids the adsorption at a given temperature and surface tension is inversely proportional to the van't Hoff factor, but it is the same for homologous fatty alcohols.

[CONTRIBUTIONS FROM THE T. JEFFERSON COOLIDGE, JR. CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF PRASEODYMIUM. THE ANALYSIS OF PRASEODYMIUM CHLORIDE.

By GREGORY PAUL BAXTER AND OLUS JESSE STEWART.

Received January 23, 1915.

CONTENTS.

Introduction. The Purification of the Praseodymium Material. The Purity of the Praseodymium Material. The Absorption Spectrum of Solutions of Praseodymium Salts. The Preparation of Praseodymium Chloride. The Purification of Silver and Reagents. The Drying of Praseodymium Chloride. The Method of Analysis. Results and Discussion.

Introduction.

Not many years ago the atomic weight of neodymium was investigated in this laboratory by the analysis of the anhydrous chloride.¹ Since considerable success was met both in preparing pure material and with the analytical method employed, the twin element praseodymium was investigated in a similar fashion; for, from the results of the earlier investigations upon praseodymium, it can readily be seen that the value of its atomic weight is far from certain.

After Auer von Welsbach² first separated the old didymium, he determined the atomic weights of the constituents by Bunsen's method of converting oxide to sulfate. Apparently the results were interchanged in publication, as Brauner has suggested, for the lower value 140.8 was assigned to neodymium.

Next Brauner,³ in 1898, starting with material purified by Shapleigh by crystallization of the double ammonium nitrate, continued the process of crystallizing this salt until neodymium was completely eliminated, then removed a trace of lanthanum by fusion with potassium nitrate, extraction of the praseodymium oxide with ammonium nitrate, and fractionation with ammonia and oxalic acid. By both the analysis of the oxalate and synthesis of the sulfate thirteen results were obtained between 140.84 and 141.19, with an average of 140.95.

Jones,⁴ in the same year, further purified double ammonium nitrate furnished by the Welsbach Light Company by crystallization until the neodymium content was about 0.06%, as determined by comparison with neodymium solutions of known concentration. Cerium was removed by the basic nitrate process, and traces of lanthanum by further crystallization of the double ammonium nitrate. Spectroscopically only a trace of lanthanum and no cerium could be detected. The oxalate was converted

¹ *Proc. Amer. Acad.*, 46, 213 (1911); *THIS JOURNAL*, 33, 1; *Z. anorg. Chem.*, 70, 1.

² *Sitzungsb. Akad. Wiss. Wien*, 92, 317 (1885).

³ *Proc. Chem. Soc.*, 1898, 70.

⁴ *Am. Chem. J.*, 20, 345 (1898).

to trioxide by ignition in air and then in hydrogen, and after being weighed the oxide was converted to sulfate. Twelve determinations between 140.38 and 140.54 gave an average of 140.46.

Schéele¹ also purified material first by crystallization of the double ammonium nitrate, next by extracting the black oxide with ammonium nitrate, and then by precipitation of the oxalate. In a final series of determinations oxalate was converted to trioxide in a current of hydrogen, and the oxide in turn to sulfate. From the ratio of trioxide to sulfate five values between 140.48 and 140.61 resulted.

In 1901, Brauner² confirmed his earlier work by four different methods, using similarly purified material. By igniting weighed quantities of octahydrated sulfate to the black oxide and correcting for the oxidizing power of the oxide as determined iodimetrically, he obtained from the ratio $\text{Pr}_2\text{O}_3 : \text{Pr}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ two results, 141.13 and 141.04. Weighed amounts of carefully dehydrated sulfate were then converted to oxide in the same way, yielding the values 140.96 and 140.94. Air-dried oxalate was weighed and ignited, and the oxidizing power of the oxide was determined. Other weighed portions of oxalate were oxidized with permanganate. The ratio $\text{Pr}_2\text{O}_3 : 3\text{C}_2\text{O}_3$ gave the average result 140.98. Finally, weighed amounts of oxalate, the praseodymium content of which had been found as above, were ignited to black oxide and this in turn to trioxide in hydrogen. The trioxide was changed to sulfate by solution in nitric acid and evaporation with sulfuric acid. Excess of acid retained by the salt was found by titration. In eight experiments the ratio $\text{Pr}_2\text{O}_3 : \text{Pr}_2(\text{SO}_4)_3$ yielded an average value 140.96. The mean of the four methods is 140.97, which is essentially identical with the result of Brauner's earlier work.

Auer von Welsbach³ next published the results of three determinations by the Bunsen method, without details, 140.64, 140.50, 140.56, average 140.57.

Finally, Feit and Przibylla⁴ purified praseodymium material from neodymium by crystallization of the double magnesium nitrate, and from lanthanum by crystallization of the nitrate from nitric acid solution. The higher oxide, prepared by ignition of the oxalate, was dissolved in standard sulfuric acid and the oxygen evolved was measured, as well as the excess of sulfuric acid. The oxygen evolved was subtracted from the weight of the black oxide before computing the atomic weight from the relation of trioxide to sulfuric acid used. The average result of three experiments is 140.54.

Thus it can be seen that while the investigations of Jones, Schéele,

¹ *Zeit. anorg. Chem.*, 17, 310 (1898).

² *Proc. Chem. Soc.*, 1901, 65; Abegg, *Handb. d. anorg. Chem.*, 3, [1] 263 (1906).

³ *Sitzungsb. Akad. Wiss. Wien*, 112, 1037 (1903).

⁴ *Zeit. anorg. Chem.*, 50, 258 (1906).

von Welsbach, and Feit and Przibylla indicate a value for the atomic weight of praseodymium between 140.5 and 140.6, that of Brauner, which was carried out with equal or greater care, and with material of undoubted purity, points to a value at least as high as 140.9. The International Committee upon Atomic Weights has chosen the lower figure, and recommends the value 140.6.

The various difficulties likely to be met in carrying out the methods used in the earlier determinations have been many times discussed, and a résumé of the situation is given in the paper by Baxter and Chapin on the atomic weight of neodymium.¹ It is worth pointing out that in addition to the dangers there mentioned, methods involving the use of praseodymium oxide are subject to error from the tendency of this substance to form a higher oxide of somewhat uncertain composition. While ignition in hydrogen causes reduction to the trioxide, yet it is not easy to make certain that no higher oxide is retained in the lower one. On the other hand, the analysis of the anhydrous chloride served so satisfactorily with neodymium that it seemed worth while to apply the same method to praseodymium. The results amply justified our expectations.

The Purification of the Praseodymium Material.

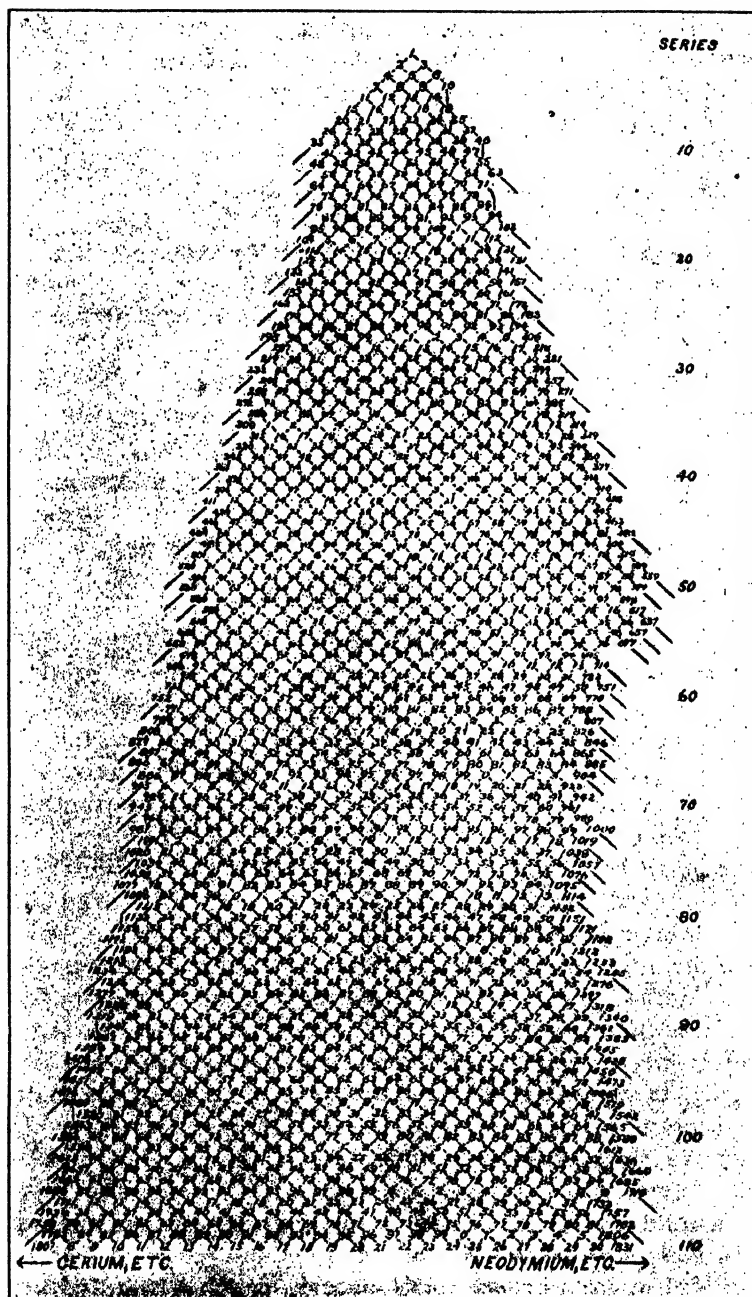
Through the great kindness of Dr. H. S. Miner, of the Welsbach Light Co., Gloucester City, N. J., we were fortunate enough to secure as a starting point about 10 kg. of praseodymium ammonium nitrate containing about 50% of the corresponding lanthanum and cerium salts as well as a small proportion of neodymium. Since one of the most rapid and effective methods of freeing praseodymium from the closely related elements, lanthanum, cerium, neodymium, and samarium, is the fractional crystallization of the above salt, this method of purification was chosen. According to Auer von Welsbach,² the bases separate in the order, lanthanum, cerium, praseodymium, neodymium, samarium, terbium and yttrium earths. The salt was crystallized in the usual way, that is, a concentrated, hot solution containing a small amount of nitric acid was allowed to cool and deposit the excess of salt, a period of 24 hours being allowed to secure equilibrium between the crystals and liquid. The separation of crystals and liquid was not completed by centrifugal drainage, because the labor and time involved in this operation are not repaid by any considerable increased speed of purification. The details of the crystallization are shown in the diagrams. In any given series of crystallizations a lower number always indicates a less soluble fraction. A line not connecting an end fraction with any fraction in a subsequent series indicates rejection. This crystallization was begun by Mr. W. H. Whitcomb,

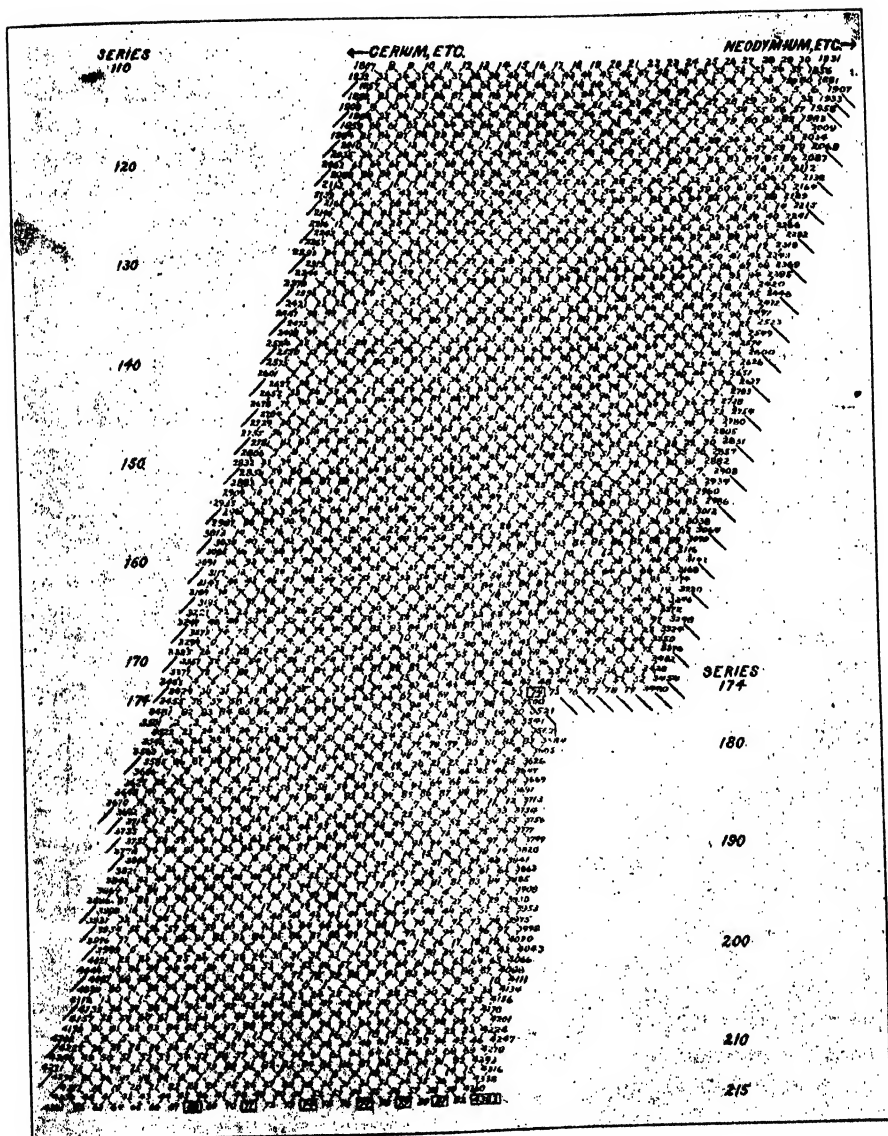
¹ *Loc. cit.*

² *Sitzungsb. Akad. Wiss. Wien*, 112, 1043 (1903).

continued by Mr. B. W. Grimes and Mr. C. C. Wallace and completed by Mr. Stewart.

In the early part of the crystallization it became obvious that the original material consisted largely of the lanthanum salt, the least soluble fraction quickly becoming essentially colorless. At the same time the neodymium absorption bands, which were readily visible in the original material, rapidly strengthened in the extreme mother liquor. When this mother liquor was reduced to a volume of about 20 cc., fraction 63, its absorption spectrum was examined visually in a Hilger wave-length spectroscope. The only absorption bands which could be detected were those of praseodymium and neodymium. No sign of any of the samarium bands could be seen. Photography of the ultraviolet absorption spectrum with a Féry quartz spectrograph also failed to indicate even a trace of samarium, for the band λ 401 was absolutely lacking. The crystallization proceeded with the occasional rejection of fairly large fractions, chiefly lanthanum and cerium, at the less soluble end of each series, and the rejection of much smaller fractions, partly neodymium, at the more soluble end, until 174 series of crystallizations had been made. From the diagrams it can be seen that the number of fractions rapidly increased from the outset to a fairly constant number between 20 and 25. In series 174 a spectroscopic examination of the more soluble fractions showed that fraction 3478 contained a very small quantity of neodymium, the absorption band at 520 being faintly visible. The proportion of neodymium in this fraction we estimate to be at least as small as 0.05%. In fraction 3476 the same neodymium band could scarcely be detected. At this point fraction 3474 was removed for analysis, since it seemed likely that this fraction was as pure as any in the series 174. The fractions 3475-3480 were rejected. Fractional crystallization was then continued in a similar way with the remaining fractions, except that while the extreme crystal fractions were occasionally rejected to remove cerium and lanthanum no fractions were rejected from the more soluble end. When the extreme fraction at this end became very small, it was set aside to be added to a subsequent similar one, and the fractionation then continued. After 41 more series of crystallizations the process was discontinued because very careful spectroscopic examination of the extreme mother liquor, fraction 4383, in saturated solution with a 10 cm. layer showed no sign of the neodymium absorption band λ 520. The quantitative examination of selected fractions was then undertaken. Those chosen were 3474, 4383, 4381, 4379, 4377, 4374, 4371 and 4368. Since the less soluble fractions beyond 4368 were believed to contain cerium, they were rejected. In fact, an analysis of fraction 4368 showed it to contain about 0.4% of this element, a proportion, however, which is hardly perceptible in the atomic weight.





The Purity of the Fractions of Praseodymium Material.

The purity of the fractions in the final series was determined as follows: In neither fraction 3474 nor the more soluble fractions of the last series, 4383 and 4381, could any of the neodymium absorption lines be detected, either visually with a Hilger wave-length spectroscop or by photography with a Hilger quartz spectrograph of the Féry type. With the latter instrument photographs were made with various depths of solution and with widely varying exposures, but the results were less satisfactory than the visual ones. In order to find out what proportion of neodymium could be detected in praseodymium material, measured portions of a standard solution of neodymium ammonium nitrate were added to weighed portions of the double ammonium nitrate of fraction 4367 which was as free from neodymium as any. By using concentrated solutions and a 10 cm. layer it was found that 0.05% of neodymium could be visually detected with ease through the absorption band λ 520, and it was evident that the sensitiveness of the method could have been increased still further if necessary. Since even 0.05% of neodymium would raise the atomic weight of praseodymium by only 0.002 unit, it is obvious that the purity of the material so far as neodymium is concerned is amply sufficient.

Attempts were made also to detect neodymium by means of the spark spectrum between copper electrodes with the quartz spectrograph, but the absence of strong neodymium emission lines at points in the praseodymium spectrum which are comparatively free from lines prevents this method from being at all satisfactory.

At the other end of the series the detection of cerium was undertaken. Since lanthanum ammonium nitrate is even less soluble than the corresponding cerium salt, the absence of cerium in the praseodymium material is sufficient proof of the absence of lanthanum also. In the spark spectrum of cerium, fortunately there is a strong line of wave length 306 located at a point in the praseodymium spectrum which is comparatively free from lines. By photographing the spectrum of the spark, between copper electrodes, of praseodymium material originally free from cerium (fraction 4380) but diluted with known percentages of cerium, it was found that the limit of detection of cerium in this way lay between 0.5 and 1.0%. Assuming the atomic weights of cerium and praseodymium to be 140.3 and 140.9, respectively, one per cent. of cerium, if in the trivalent condition, would lower the atomic weight of praseodymium by 0.006 unit. Such a difference is difficult to detect by the method which we are using for the determination of the atomic weight of praseodymium. Upon photographing the spark spectra of the extreme fractions 4361, 4364 and 4368 (the most impure analyzed), it was found by comparison that the first fraction of the three was rich in cerium, the second contained much less, and fraction 4368 contained no more at any rate than 1%

Because of the uncertainty in estimating proportions of impurity from the intensity of the spectrum lines, fractions 4365, 4368, and 4371 were further tested for cerium as follows: The solution was precipitated with an excess of sodium hydroxide and the precipitated hydroxides were washed several times. Carefully scrubbed chlorine gas was next passed into the solution in order to dissolve the praseodymium hydroxide. The residual ceric hydroxide was dissolved and the process was repeated. The second residue was collected upon a filter paper, washed and ignited. Then the dissolved praseodymium was precipitated as oxalate and ignited to oxide which was weighed. In this way fraction 4365 was found to contain 2.5%, fraction 4368, 0.4% and fraction 4371, 0.1% of cerium. Besides the small and unimportant percentage of cerium in fractions 4368 and 4371, which were analyzed, the rapid falling off of the cerium percentage is worth noting.

The Absorption Spectrum of Praseodymium Chloride.

The absorption spectrum of praseodymium chloride prepared from fraction 4181 was measured in the region of the visible spectrum by means of a Hilger wave-length spectroscop, provided with an extra dense prism and achromatic lenses. The accuracy of measurement with this spectroscop was not far from $0.1 \mu\mu$ even for the longer wave lengths. Of the four broad absorption bands shown by concentrated solutions, only the one in the yellow visibly resolves into two narrower ones as the dilution increases. The wave lengths of the middle of each band at the lowest concentration at which it could be plainly seen are given below, together with observations by some other observers.¹ Praseodymium nitrate was found to give an exactly similar absorption spectrum.

| Baxter and Stewart. (1914). | Aufrecht. (1904). | Auer. (1903). | Böhm. (1902). |
|--------------------------------|----------------------|------------------|------------------|
| 597 | 595.5 | 596 | ... |
| 587 | 590.1 | 592-587 | 589.6 |
| 481.5 | 482.0 | 482-481 | 481.2 |
| 469 | 468.9 | 470.6-466.2 | 469.0 |
| 443.5 | 444.0 | 447.8-440.3 | 444.0 |

Photographs of the absorption spectrum also were taken with a Féry quartz spectrograph. When the source of illumination was a Nernst filament, no absorption bands beyond the visible region could be found with any exposure or any concentration of solution. When the spark from "Nichrome" wire was employed, however, it was found that the light is completely cut off at from λ 280 to λ 270 according to the concentration of the solution, and that the solution is opaque up to the extreme limit of the spectrograms, about λ 210. In these spectrograms there were noticeable at certain concentrations very faint minima of absorption in the middle of all three bands in the blue. These minima

¹ Kayser, *Handb. d. Spectr.*, 3, 440.

could be seen over a considerable range of concentration in all three cases but the particular concentration at which they were most marked was different for the three bands. Measurements were made of the position of these minima with a comparator and the cadmium spark spectrum as a standard, and the minima were found to coincide with the centers of the absorption bands observed with the most dilute solutions both visually and in the spectrograms.

The ultraviolet absorption bands at 354 and 353 reported by Forsling¹ and the one at 346 given by Exner² correspond to strong absorption bands of neodymium. As we could not find the least trace of these bands in the spectrograms, it seems probable that they were produced by neodymium impurity.

The Preparation of Praseodymium Chloride.

Each fraction of double nitrate investigated was converted to chloride as follows: The salt was dissolved, and the solution, after dilution to about two liters, was filtered. A considerable quantity of nitric acid was added, the solution was heated to boiling and praseodymium oxalate was precipitated by an excess of oxalic acid. After the precipitate had been thoroughly washed by decantation, it was collected upon a disk of filter paper in a large porcelain Gooch crucible, and dried in an electric oven at 105°. In order to change the oxalate to oxide it was heated to dull redness in a platinum boat in an electrically heated porcelain muffle. Care was taken that the temperature should not be high enough to vaporize platinum from the boat into the oxide.³ The black oxide was next dissolved in a quartz dish in a large excess of nitric acid which had been distilled through a quartz condenser, and the oxalate was reprecipitated from dilute solution by adding a solution of twice recrystallized ammonium oxalate. After thorough washing, the oxalate was collected, dried and ignited as before. The chloride was now prepared by dissolving the oxide in a quartz dish in hydrochloric acid which had been distilled through quartz. Free chlorine was expelled by heating on an electric stove, and the salt was crystallized three or four times from concentrated solution by "salting out" at 0° with hydrochloric acid gas made by boiling the fuming solution and conducting the gas to the solution through a quartz tube. The crystals were each time centrifugally drained and rinsed in platinum Gooch crucibles.⁴ The product was preserved in quartz in a vacuum desiccator over fused potassium hydroxide.

The Purification of Silver and Reagents.

The greater part of the silver used in this work was prepared by Mr. W. H. Whitcomb for an investigation upon the atomic weight of neo-

¹ Kayser, *Loc. cit.*

² *Ibid.*

³ See Baxter and Chapin, *THIS JOURNAL*, 33, 16 (1911).

⁴ Baxter, *THIS JOURNAL*, 30, 286 (1908).

dymium, which will be published shortly. No innovations were made in the processes of purification which have been frequently described in papers from the Harvard Laboratory. These processes were in brief as follows: Crude silver was dissolved in nitric acid, and the chloride was precipitated with a large excess of hydrochloric acid. The precipitate, after being washed, was dissolved in ammonia and reprecipitated with nitric acid. Then the silver chloride was reduced with sodium hydroxide and sugar, and the metal was fused on charcoal before a blast lamp. The metallic buttons were cleansed by scouring and etching, dissolved in distilled nitric acid, and the metal reprecipitated with ammonium formate made from distilled ammonia and formic acid. After thorough washing the product was again fused on the purest lime before a blast lamp. Electrolytic deposition, with silver nitrate as the electrolyte and with a dissolving anode of the pure silver buttons, followed and the electrolytic crystals were fused in a current of electrolytic hydrogen on a pure lime boat. Adhering lime was removed by etching with nitric acid, and the buttons were washed with water and ammonia, dried, and heated to about 500° in a vacuum. The silver was preserved over potassium hydroxide in a desiccator. In some of the later analyses the silver used had been purified exactly as described above by Mr. F. L. Grover for work upon the atomic weight of lead, or by Dr. H. C. Chapin for the investigation upon neodymium.

In Analyses 1 and 2 silver nitrate was employed which had been freed from chloride by repeated crystallization. This material was prepared by Dr. Grinnell Jones for work on the atomic weight of phosphorus.¹

In the preparation of reagents the precautions usual in exact work were taken. The ordinary distilled water of the laboratory was twice redistilled, once from alkaline permanganate and once alone, through block-tin condensers. Hydrochloric and nitric acids were distilled through quartz condensers, in the case of the hydrochloric acid the first and last running being rejected, in the case of the nitric acid two distillations being carried out, the first third being rejected in each distillation. Nitric acid distilled in this way does not contain more than the merest trace of chlorine, if the original acid is nearly free from the latter element.

Quartz or platinum utensils were employed wherever glass would have introduced objectionable impurities, and electrical heaters were used whenever the products of combustion of illuminating gas were to be avoided. In the crystallization of solids centrifugal drainage was always used to assist in the mechanical removal of mother liquor from crystals, except in the fractional crystallization of the praseodymium material where it would have been of little assistance.

¹ *Proc. Amer. Acad.*, 45, 137 (1909); *THIS JOURNAL*, 31, 298.

The Drying of Praseodymium Chloride.

The drying of the chloride for analysis was effected according to the recommendations of Matignon¹ and in very much the same way that neodymium chloride was dried by Baxter and Chapin, except that while the neodymium salt was not fused, and hence retained a trace of water, which was subsequently determined, the praseodymium chloride was rendered anhydrous by fusion. Bearing in mind the earlier experience with neodymium chloride, that the dehydration of the salt must be made as complete as possible before the actual fusion occurs, in order to prevent the formation of basic salt, the salt was caused to lose its crystal water by a process of efflorescence in a current of dry nitrogen and hydrochloric acid gases at gradually increasing temperatures. Richards² has pointed out that a hydrated salt may be freed from moisture much more effectively in this way than when melting is allowed to take place. We found the transition temperature of the heptahydrate³ to be 111° but when the salt is heated in a current of hydrochloric acid gas, the melting point is somewhat lowered. Therefore, until a very considerable proportion of the water had been expelled, the temperature was kept below 100° . The temperature was then raised to about 165° where the last molecule of crystal water begins to evaporate, according to Matignon,⁴ and when the salt was essentially anhydrous it was gradually heated to about 350° . During the latter part of the heating only hydrochloric acid was passed through the tube. The aluminum block oven⁵ which had been used for heating the salt up to this point was now replaced by a sleeve which could be heated electrically and the salt was first heated to dull redness for a few minutes and then quickly to its fusing point, which Matignon⁶ states to be 818° .

The platinum boat with the salt was placed in a quartz tube which formed part of the "bottling apparatus"⁷ containing the weighing bottle with its stopper in which the boat originally had been weighed, and the bottling apparatus was connected with systems for the production of pure dry hydrochloric acid, nitrogen, and air. The hydrochloric acid gas was generated by adding c. p. concentrated sulfuric acid to c. p. fuming hydrochloric acid, and the gas was dried by passing through five towers filled with beads moistened with concentrated sulfuric acid which had previously been heated nearly to its boiling point. Nitrogen was prepared by Wanklyn's method of saturating air with ammonia and passing the mixture over

¹ *Compt. rend.*, **134**, 427 (1902).

² *Z. physik. Chem.*, **46**, 194 (1903).

³ Matignon found 105° . *Loc. cit.*

⁴ *Loc. cit.*

⁵ *Proc. Amer. Acad.*, **44**, 184 (1909); *THIS JOURNAL*, **31**, 206.

⁶ *Compt. rend.*, **140**, 1340 (1905).

⁷ Richards and Parker, *Proc. Amer. Acad.*, **32**, 59 (1896).

hot copper gauze. The excess of ammonia was removed by dilute sulfuric acid, and the nitrogen was further purified and dried in towers containing glass beads moistened with silver nitrate solution, fused potassium hydroxide, concentrated sulfuric acid, and phosphorus pentoxide. Nitrogen made in this way invariably contains a small proportion of hydrogen,¹ owing to catalytic decomposition of the excess of ammonia on the copper tube, but this gas would do no harm in the present instance. Air was purified and dried by reagents similar to those used for purifying the nitrogen. The apparatus was constructed wholly of glass with either ground or fused joints, except at the beginning of the air and nitrogen apparatus. By means of stopcocks any one of the three gases could be delivered to the bottling apparatus at will. This apparatus is identical with that used by Baxter and Hartmann² for the drying of cadmium chloride, and by Baxter and Grover³ for the drying of lead chloride. After the fusion of the neodymium chloride, the hydrochloric acid was displaced by nitrogen and the nitrogen in turn by air. Then the boat and contents were transferred to the weighing bottle, which was allowed to stand in a desiccator near the balance for some hours before being weighed.

A solution of praseodymium chloride, which has been fused in this way, sometimes contains a small amount of insoluble glistening particles, practically invisible unless examined in a strong light in a vessel whose curvature magnifies their apparent size. A similar difficulty was met by Baxter and Chapin in the preparation of pure anhydrous neodymium chloride. Under unfavorable conditions, which will be described shortly, the amount of this insoluble material may be considerably augmented, but when prepared under the most favorable conditions the salt dissolves rapidly without leaving even a trace of insoluble matter. Even when a small amount of insoluble material is formed, a clear solution is usually obtained after a day or two. The conditions under which the extent of the difficulty is too small to have an appreciable effect upon the results, have been found to be very careful preliminary dehydration of the salt, and a very short period of fusion. These conditions were maintained in the preparation of all of the specimens of material which were analyzed, but only in Analyses 5, 6, 9, 10, 16, 24, 25, 30, 31, 38 and 39 was the solution of the salt absolutely clear at the start.

Many experiments were carried out, however, first, to find out the nature of the insoluble matter, and second, to discover the extent of the difficulty. At the outset there seemed to be three possibilities as to the nature of the substance. The most probable one was that the substance is a basic

¹ Dr. R. C. Wells first pointed out this fact to us.

² THIS JOURNAL, 37, 113 (1915).

³ Investigation not yet published.

chloride, but it was possible that it might be either an insoluble allotropic form of the trichloride or a lower chloride, *i. e.*, praseodymium dichloride. The fact that prolonged fusion of the salt invariably resulted in the formation of relatively large amounts of insoluble material seemed to point toward one of the last two explanations, although there seems to be no certain evidence of the existence of such compounds in the case either of praseodymium or of other rare earths.

In order to find out the composition of the insoluble substance, amounts large enough to be analyzed were prepared by dehydrating the crystals with the usual care, and then fusing the salt for periods from one-half hour to one hour in a current of dry hydrochloric acid gas. The product was then treated with water, and as soon as the soluble portion of the salt had dissolved, the insoluble residue was collected upon a small weighed platinum-sponge Gooch crucible, dried and weighed. The residue, which was distinctly crystalline, did not change in appearance during the drying, so that it is improbable that its composition was appreciably altered during this treatment. The praseodymium content of the residue was then determined by dissolving the residue from the crucible in dilute hydrochloric acid, precipitating the base with ammonium oxalate, collecting the precipitate upon a filter, and igniting in a weighed platinum boat. The weight of the black oxide Pr_2O_3 was checked by igniting the residue in a stream of hydrogen and reweighing. The weights of oxide obtained in two experiments correspond very closely to the weight which should be obtained, assuming the residue to be praseodymium oxychloride, PrOCl . About 6 g. of anhydrous salt were used in each experiment.

| Period of fusion. Min. | Gram insoluble residue. | Gram Pr_2O_3 observed. | Gram Pr_2O_3 calc. from PrOCl . | Gram Pr_2O_3 calc. from PrCl_3 . | Gram of Pr_2O_3 calc. from PrCl_3 . | Gram of Pr_2O_3 calc. from PrOCl . |
|---------------------------|-------------------------|--|--|---|--|---|
| 35 | 0.2002 | 0.1760 | 0.1757 | 0.1366 | 0.1597 | 0.1700 |
| 60 | 0.0131 | 0.0117 | 0.0115 | 0.0090 | 0.0104 | 0.0114 |

The composition of the residue was further checked by determining the chlorine content. Residues were collected and weighed as above, and then after solution in dilute nitric acid, the chlorine was precipitated as silver chloride, collected and weighed. During the solution of the residue the crucible and contents were placed in a closed tube through which a current of air was passed into a solution of ammonia, so that in case chlorine was liberated during the solution, it would be caught in the ammonia. The results of the chlorine determinations check closely those of the praseodymium determinations.

| Period of fusion. Min. | Gram insoluble residue. | Gram AgCl observed. | Gram AgCl calc. from PrOCl . | Gram AgCl calc. from PrCl_3 . | Gram AgCl calc. from PrCl_3 . |
|---------------------------|-------------------------|------------------------------|--|---|---|
| 60 | 0.0146 | 0.0110 | 0.0109 | 0.0252 | 0.0198 |
| 60 | 0.0111 | 0.0079 | 0.0083 | 0.0193 | 0.0150 |

Since it is obvious that, if the oxychloride is formed from the trichloride, a loss in weight must occur, further experiments were carried out to discover whether during the formation of the larger amounts of insoluble residue, when the fusion is prolonged, the loss in weight of the salt corresponds to the weight of residue produced. In these experiments the hydrated salt was first very carefully dried, then quickly fused and weighed. During this treatment little, if any, insoluble material is formed. Then the boat with the salt was returned to the quartz tube, and after the apparatus had been thoroughly swept out with dry hydrochloric acid, the salt was brought to the fusing temperature, which was maintained for one hour in every case. After the salt had been reweighed, the insoluble residue was determined as previously described and a few tenths of a milligram of salt which sublimed from the boat to the quartz tube were dissolved in water, the solution was evaporated and the residue was heated and weighed. The weight of sublimed material was of course added to the weight of the fused salt before determining the loss in weight during fusion.

| Period of fusion. Min. | Loss on fusion. | Gram of insoluble residue observed. | Gram of insol. residue calc. as PrOCl . | Gram of insol. residue calc. as PrCl_3 . |
|------------------------------|--------------------|---|--|---|
| 60 | 0.0063 | 0.0234 | 0.0220 | 0.0376 |
| 60 | 0.0034 | 0.0111 | 0.0119 | 0.0203 |

These experiments agree very satisfactorily with those in which the praseodymium and chlorine were actually determined, in indicating beyond question that the insoluble residue is the oxychloride.

The surprising feature of these results is that the amount of insoluble matter increases with the period of fusion instead of decreasing or even remaining constant. The obvious conclusion is that some source of oxygen exists in the fusion atmosphere. To be sure, in the first of the experiments for the determination of the insoluble residue a tiny hole was discovered in one of the fused joints of the hydrochloric acid apparatus, and in this experiment the weight of insoluble residue was found to be about ten times as large as in the subsequent experiments. Fortunately the defective joint was a comparatively new one, and could have affected only four of the fusions of the salt for analyses. The analyses involved are Nos. 12, 13, 14, 15, 34, 35, 36 and 37. The hole was excessively small, however, and it is not at all certain that any real difficulty was produced. It seemed possible that the hydrochloric acid gas might contain air, originating in the reagents used for generating the gas, or possibly from incomplete sweeping out of the purifying train. By passing the hydrochloric acid gas into water under an inverted tube after the apparatus had been thoroughly swept out, we found that it actually did contain a trace of air. We tried in some experiments to avoid the first difficulty by passing the hydrochloric acid gas through a hydrochloric acid solution of cuprous

chloride before it entered the drying towers, and in order to avoid the second difficulty the apparatus was swept out even longer than before previous to the fusion of the salt, but neither of these remedies seemed to have any effect upon the formation of the basic salt. Another source of oxygen might be moisture. However, concentrated sulfuric acid has been found by Morley¹ to be a very effective drying agent. One liter of gas passed over concentrated sulfuric acid retains only 0.003 mg. of moisture. In order to make sure that the hydrochloric acid was really as dry as this, the gas was passed for several hours through a U-tube cooled with alcohol and solid carbon dioxide. A very small amount of white solid was condensed in the tube, presumably a hydrate of hydrochloric acid. But even on the assumption that all of the moisture is removed from the gas by the salt during the fusion, it seems impossible that the residue should have formed wholly from moisture contained by the acid gas. Still another possibility was that the quartz tube was attacked by the acid gas to yield moisture and a chloride of silicon. This point was tested by drying and fusing the salt in a platinum tube instead of in a quartz tube, but even under these conditions the insoluble residue was formed. We are still somewhat uncertain as to the cause of the formation of the basic salt during prolonged fusion, although incomplete preliminary drying is invariably the cause when the fusion period is short, but we are inclined to the opinion that the difficulty is due to a trace of air in the hydrochloric acid gas.

Since we were unable to avoid the formation of the insoluble material in every case, in two experiments in which the salt was dried as for analysis and then fused for a short period, the insoluble residue was collected and weighed. The results of these experiments follow. As before, about 6 g. of anhydrous salt were used in each experiment.

| | | |
|-------------------------------|-----------|-----------|
| Period of fusion..... | 0.5 min. | 4 min. |
| Wt. of insoluble residue..... | 0.0001 g. | 0.0010 g. |

In order to discover whether the basic salt dissolves to an appreciable extent, in experiments with three separate portions of material which had been collected, dried and weighed upon a platinum-sponge crucible, about a liter of water was allowed to flow slowly through the crucible during the course of an hour. The crucible and contents were then dried and reweighed. The losses in weight per liter of water were 0.9, 0.5 and 0.3 mg. While these figures are undoubtedly somewhat less than the real solubility in water, they are probably far greater than the solubility in dilute praseodymium chloride solution. This explains the extreme slowness with which a mere trace of the basic salt dissolves in the solution of the neutral salt and supports the conclusion that the quantity of basic salt present in the material fused for a short time is very small.

¹ *Am. J. Sci.*, 30, 141 (1885).

In preparing the salt for the actual analyses the period of fusion was less than one minute, so that the weight of residue certainly must have been considerably less than 1 mg. But since even as large a proportion as 1 mg. of oxychloride in 5 g. of salt, if it dissolves eventually, would raise the apparent atomic weight of praseodymium by only 0.028, we feel that little danger is introduced by not attempting to apply any correction for the residue.

In a research upon the atomic weight of neodymium carried out immediately at the conclusion of this research, similar evidence was obtained as to the nature of the insoluble neodymium compound which forms under essentially the same conditions.

The Method of Analysis.

After the salt had been fused and weighed, the boat was transferred to a glass-stoppered Erlenmeyer flask and treated with about 500 cc. of pure water. In eleven of the analyses the salt dissolved immediately, leaving an absolutely clear solution. In the remainder of the analyses, after the bulk of the salt was in solution, by close inspection a small quantity of the insoluble basic chloride could be seen. On allowing the flask to stand for a considerable period, 24 to 48 hours in general, this basic salt disappeared, and in a few instances gentle heating was used to accelerate its solution. When the solution was clear, it was transferred quantitatively to the 3 or 4 liter glass-stoppered Erlenmeyer precipitating flask. The rinsings of the weighing bottle were added and the solution diluted to a volume of from 1200 to 1500 cc. In the meantime a quantity of pure silver as nearly as possible equivalent to the praseodymium chloride was dissolved in nitric acid, in a dissolving flask provided with a column of bulbs to prevent loss by spattering while the metal was dissolving. After diluting the solution of silver nitrate, it was heated to eliminate nitrous acid, and then further diluted to about the same volume as the praseodymium chloride solution. The silver nitrate solution was poured into the chloride solution, both being cold, in small portions with continual gentle agitation. When the silver nitrate had been completely transferred to the precipitating flask, the flask was stoppered and gently shaken to insure thorough mixing, and allowed to stand for several days with occasional shaking. Then it was cooled with ice water in order to lower the solubility of the silver chloride, and after standing for a day in the ice bath, portions of the mother liquor were tested for excess of silver or chloride by adding to separate portions equal amounts of 0.01 N chloride and silver solutions and comparing the opalescences in a nephelometer. If a deficiency of either chloride or silver was found, this deficiency was made up by adding 0.01 N silver or chloride solution. The amount of either added, expressed in the silver equivalent, is given in the tables of results under the heading "Silver added or subtracted." When

equilibrium had been reached, 0.05 g. of dissolved silver nitrate for each liter of supernatant liquid was added to render the silver chloride less soluble. After the solution had been allowed to stand for at least a day, usually much longer, at room temperature, the precipitate was washed many times by decantation with a solution containing 0.05 g. of silver nitrate per liter, and several times with ice-cold water, and transferred with cold water to a large weighed platinum-sponge Gooch crucible. The crucible with its contents was dried for at least 12 hours in an electric air bath at 160° , cooled in a desiccator and weighed. The crucible had originally been dried in exactly the same way. In order to find out how much moisture had been retained by the dried silver chloride, the greater part of the salt was transferred to a porcelain crucible which was weighed. Then the crucible was heated to the fusing point of the silver chloride and reweighed. The loss in weight is assumed to represent residual moisture. On an average 0.004 % of moisture was found, a proportion which is in accord with earlier experience in the Harvard laboratories.

The solubility of silver chloride in the filtrate and silver nitrate wash waters, which both contained 0.05 g. of silver nitrate per liter, was computed from the solubility products as found by Kohlrausch¹ at 20° and 25° , 1×10^{-10} and 1.7×10^{-10} , respectively. At 20° the solubility in 0.0003 *N* silver nitrate solution is 0.05 mg., at 25° 0.08 mg. per liter. The former correction was used during the colder months when the laboratory was maintained at about 20° , the latter correction in four analyses which were completed in summer. The total correction in most cases fell between 0.2 and 0.3 mg. The silver chloride dissolved in the aqueous rinsings as well as that obtained by rinsing the precipitating flask with ammonia was determined by comparison with standard solutions of chloride in a nephelometer, the usual precautions being taken to secure uniformity of precipitation. As in earlier researches it was found desirable to dissolve in ammonia the cloud of silver chloride in both the standard solution and that being analyzed, and then to reprecipitate with nitric acid.

Corrections were of course applied for any chloride introduced in order to compensate for excess of silver, and also for the standard chloride solution added to the portions which were tested in the comparison, for these portions were always returned to the precipitating flask. The latter quantity amounts to 1.328 mg. for each test which was made in the comparison. Because of the comparatively large size of this correction, the standard silver and chloride solutions were made up, preserved, and measured with great care.

Weighings were carried out on a No. 10 Troemner balance, sensitive at least to 0.02 mg. In order to avoid difficulties from changes in at-

¹ *Z. physik. Chem.*, 64, 167 (1908).

nospheric humidity and density, the receptacles containing the salts were always weighed by substitution for counterpoises as nearly as possible like the objects both in material, volume, and external surface. The balance case was provided with a small amount of radioactive material to dissipate electrical charges produced during the transference of the objects to the balance pans. The weights were standardized to hundredths of a milligram by the method described by Richards.¹ Vacuum corrections were applied as follows:

| | Specific gravity. | Vacuum correction per gram. |
|-------------------------|--------------------|-----------------------------|
| Weights..... | 8.3 | |
| PrCl ₃ | 4.020 ² | +0.000154 |
| AgCl..... | 5.56 | +0.000071 |
| Ag..... | 10.49 | -0.000031 |

THE ATOMIC WEIGHT OF PRASEODYMIUM.

 Series I. PrCl₃ : 3AgCl.

Ag = 107.880.

Cl = 35.457.

| No. of anal. Frac- tion. | Grams of PrCl ₃ in vacuum. | Grams of AgCl in vacuum. | Loss on fusion. | Dissolved AgCl. | Corrected weight of AgCl in vacuum. | Ratio PrCl ₃ : 3AgCl. | Atomic weight of praseo- dymium. |
|-----------------------------|---|--------------------------------|--------------------|--------------------|--|--|---|
| 1 3474 | 4.12848 | 7.17753 | 0.00004 | 0.00166 | 7.17915 | 0.575065 | 140.913 |
| 2 3474 | 6.91605 | 12.02366 | 0.00016 | 0.00183 | 12.02533 | 0.575123 | 140.939 |
| 3 3474 | 7.66554 | 13.32562 | 0.00023 | 0.00392 | 13.32931 | 0.575089 | 140.923 |
| 4 3474 | 5.01155 | 8.71232 | 0.00026 | 0.00173 | 8.71379 | 0.575128 | 140.941 |
| | | | | | Av., | 0.575101 | 140.929 |
| 5 4383 | 6.04235 | 10.50645 | 0.00027 | 0.00126 | 10.50744 | 0.575054 | 140.909 |
| 6 4383 | 6.14745 | 10.68933 | 0.00029 | 0.00146 | 10.69050 | 0.575039 | 140.902 |
| | | | | | Av., | 0.575047 | 140.906 |
| 7 4381 | 6.32550 | 10.99679 | 0.00030 | 0.00206 | 10.99855 | 0.575121 | 140.937 |
| 8 4381 | 4.59463 | 7.98763 | 0.00022 | 0.00199 | 7.98940 | 0.575090 | 140.925 |
| | | | | | Av., | 0.575106 | 140.931 |
| 9 4379 | 5.96661 | 10.37370 | 0.00040 | 0.00224 | 10.37554 | 0.575065 | 140.913 |
| 10 4379 | 6.87536 | 11.95356 | 0.00030 | 0.00182 | 11.95508 | 0.575100 | 140.928 |
| | | | | | Av., | 0.575083 | 140.921 |
| 11 4377 | 4.64585 | 8.07649 | 0.00052 | 0.00161 | 8.07758 | 0.575154 | 140.951 |
| 12 4374 | 6.85492 | 11.91575 | 0.00000 | 0.00199 | 11.91774 | 0.575186 | 140.965 |
| 13 4374 | 8.01711 | 13.93737 | 0.00008 | 0.00224 | 13.93953 | 0.575135 | 140.943 |
| 14 4374 | 6.17045 | 10.72789 | 0.00005 | 0.00049 | 10.72833 | 0.575155 | 140.952 |
| 15 4374 | 6.90040 | 11.99805 | 0.00022 | 0.00163 | 11.99946 | 0.575059 | 140.911 |
| 16 4374 | 7.08498 | 12.31948 | 0.00043 | 0.00114 | 12.32019 | 0.575071 | 140.916 |
| | | | | | Av., | 0.575121 | 140.937 |
| 17 4371 | 6.20845 | 10.79439 | 0.00003 | 0.00116 | 10.79552 | 0.575095 | 140.926 |
| 18 4371 | 7.07590 | 12.30310 | 0.00025 | 0.00116 | 12.30401 | 0.575089 | 140.924 |
| | | | | | Av., | 0.575092 | 140.925 |
| 19 4368 | 5.77646 | 10.04305 | 0.00021 | 0.00119 | 10.04403 | 0.575113 | 140.935 |
| 20 4368 | 5.72002 | 9.94547 | 0.00021 | 0.00125 | 9.94651 | 0.575078 | 140.919 |
| | | | | | Av., | 0.575096 | 140.927 |

¹ THIS JOURNAL, 22, 144 (1900).

² Determined at 25° by Mr. C. F. Hawkins, not yet published. Matignon found 4.017 at 18°. *Compt. rend.*, 140, 1340 (1905).

THE ATOMIC WEIGHT OF PRASEODYMIUM.

Series II. $\text{PrCl}_3 : 3\text{Ag}$.

| Ag = 107.880. | | | | | Cl = 35.457. | | |
|--------------------------|----------------|---|------------------------------|--------------------------|--|------------------------------------|--------------------------------------|
| No. of anal- ysis. | Frac- tion. | Grams of PrCl_3 in vacuum. | Grams of Ag in vacuum. | Grams of Ag added. | Corrected weight of Ag in vacuum. | Ratio PrCl_3 : 3Ag. | Atomic weight of praseodymium. |
| 21 | 3474 | 7.66554 | 10.02872 | 0.00257 | 10.03129 | 0.764163 | 140.943 |
| 22 | 3474 | 8.78959 | 11.49955 | 0.00356 | 11.50311 | 0.764106 | 140.924 |
| 23 | 3474 | 5.01155 | 6.55888 | 0.00010 | 6.55898 | 0.764075 | 140.914 |
| | | | | | Av., | 0.764115 | 140.927 |
| 24 | 4383 | 6.04235 | 7.90826 | —0.00006 | 7.90820 | 0.764061 | 140.910 |
| 25 | 4383 | 6.14745 | 8.04493 | 0.00070 | 8.04563 | 0.764073 | 140.914 |
| | | | | | Av., | 0.764067 | 140.912 |
| 26 | 4381 | 6.32550 | 8.27440 | 0.00446 | 8.27886 | 0.764054 | 140.908 |
| 27 | 4381 | 5.12982 | 6.71246 | 0.00113 | 6.71359 | 0.764095 | 140.920 |
| 28 | 4381 | 4.59463 | 6.01206 | 0.00125 | 6.01331 | 0.764077 | 140.915 |
| 29 | 4381 | 4.77556 | 6.24933 | 0.00061 | 6.24994 | 0.764097 | 140.921 |
| | | | | | Av., | 0.764081 | 140.916 |
| 30 | 4379 | 5.96661 | 7.80878 | 0.00030 | 7.80908 | 0.764060 | 140.910 |
| 31 | 4379 | 6.87536 | 8.99794 | 0.00030 | 8.99824 | 0.764079 | 140.915 |
| | | | | | Av., | 0.764070 | 140.913 |
| 32 | 4377 | 5.73602 | 7.50710 | —0.00003 | 7.50707 | 0.764082 | 140.917 |
| 33 | 4377 | 4.64585 | 6.08004 | 0.00025 | 6.08029 | 0.764084 | 140.917 |
| | | | | | Av., | 0.764083 | 140.917 |
| 34 | 4374 | 6.85492 | 8.97128 | 0.00020 | 8.97148 | 0.764079 | 140.916 |
| 35 | 4374 | 8.01711 | 10.49205 | 0.00045 | 10.49250 | 0.764080 | 140.916 |
| 36 | 4374 | 6.17045 | 8.07517 | —0.00092 | 8.07425 | 0.764214 | 140.959 |
| 37 | 4374 | 6.90040 | 9.03078 | —0.00014 | 9.03064 | 0.764110 | 140.926 |
| 38 | 4374 | 7.08498 | 9.27297 | —0.00023 | 9.27274 | 0.764065 | 140.911 |
| 39 | 4374 | 5.81310 | 7.60811 | 0.00000 | 7.60811 | 0.764066 | 140.911 |
| | | | | | Av., | 0.764102 | 140.923 |
| 40 | 4371 | 6.20845 | 8.12468 | 0.00073 | 8.12541 | 0.764079 | 140.915 |
| 41 | 4371 | 7.07590 | 9.26026 | 0.00019 | 9.26045 | 0.764099 | 140.922 |
| | | | | | Av., | 0.764089 | 140.919 |
| 42 | 4368 | 5.77646 | 7.56013 | —0.00013 | 7.56000 | 0.764082 | 140.916 |
| 43 | 4368 | 5.72002 | 7.48696 | —0.00100 | 7.48596 | 0.764100 | 140.922 |
| | | | | | Av., | 0.764091 | 140.919 |

Results and Discussion.

In order to show that no considerable error occurred, owing either to occlusion by silver chloride or from loss of silver chloride in solution, the ratio between the silver used and the silver chloride obtained has been calculated in the eighteen pairs of analyses for which the data are available.

The average ratio of silver to silver chloride is within less than four thousandths of a per cent. of that obtained by Richards and Wells,¹ 0.752634 : 1.000000. Part of the discrepancy is due to the fact that in a few analyses, notably Nos. 12, 13 and 14, the platinum-sponge crucible allowed traces of solid silver chloride to pass through. The difficulty

¹ *Pub. Car. Inst.*, No. 28 (1905); *THIS JOURNAL*, 28, 456.

| Analyses. | Ag: AgCl. |
|-----------|-----------|
| 3 and 21 | 0.752573 |
| 4 and 23 | 0.752711 |
| 5 and 24 | 0.752628 |
| 6 and 25 | 0.752597 |
| 7 and 26 | 0.752723 |
| 8 and 28 | 0.752660 |
| 9 and 30 | 0.752644 |
| 10 and 31 | 0.752671 |
| 11 and 33 | 0.752735 |
| 12 and 34 | 0.752784 |
| 13 and 35 | 0.752716 |
| 14 and 36 | 0.752610 |
| 15 and 37 | 0.752587 |
| 16 and 38 | 0.752647 |
| 17 and 40 | 0.752664 |
| 18 and 41 | 0.752637 |
| 19 and 42 | 0.752685 |
| 20 and 43 | 0.752630 |

Average, 0.752661

was not detected in time to determine the extent of the error, but in one of these analyses silver chloride was found to have settled out of the mother liquor on long standing. This is undoubtedly the reason why the atomic weight of praseodymium determined in these analyses is slightly higher than in most other experiments. Needless to say, the crucible was repaired and in Analyses 15 and 16, made subsequently with the same fraction of material as Analyses 12, 13 and 14, the results are in accord with the general mean of all the determinations. These defective analyses as well as a very few other discrepant determinations, have not been omitted in computing averages, since, because of the large number of experiments, their influence is not large.

RESULTS AVERAGED BY FRACTIONS.

| Fraction. | PrCl ₃ : 3Ag. | PrCl ₃ : 3AgCl. | Average of individual determinations. | Average corrected for cerium content. |
|-----------|--------------------------|----------------------------|---------------------------------------|---------------------------------------|
| 3474 | 140.927 | 140.929 | 140.928 | 140.928 |
| 4383 | 140.912 | 140.906 | 140.909 | 140.909 |
| 4381 | 140.916 | 140.931 | 140.921 | 140.921 |
| 4379 | 140.913 | 140.921 | 140.917 | 140.917 |
| 4377 | 140.917 | 140.951 | 140.928 | 140.928 |
| 4374 | 140.923 | 140.937 | 140.930 | 140.930 |
| 4371 | 140.919 | 140.925 | 140.922 | 140.923 |
| 4368 | 140.919 | 140.927 | 140.923 | 140.925 |

Average, 140.923
Average of all Individual Determinations, 140.924

When the results are averaged by fractions, further evidence is added to

that obtained by the spectroscope, that all the fractions analyzed were of a high degree of purity.

Fraction 4383, which contained all the neodymium which may have accumulated in forty-one series of crystallizations, gives a slightly lower instead of higher figure than the average, while fraction 4368 which contained more cerium than any other fraction gives a result identical with the average. This close similarity is very striking when one considers that a range of sixteen fractions is included in those examined. Fraction 3474, selected at an earlier stage of the fractionation as being very pure, also shows no sign of being different from the other fractions.

The foregoing results leave little opportunity for choice. There seems to be no reason for preferring the value obtained with any one or more fractions to those resulting with the others. Possibly the average of Analyses 5, 6, 9, 10, 16, 24, 25, 30, 31, 38 and 39, 140.913, is more reliable than the average of all, for in these analyses the praseodymium chloride dissolved rapidly and completely at the start, and was probably entirely free from basic salt, but we believe that the final corrected average of all the experiments, 140.92, represents fairly the best material we succeeded in preparing. This result is not far from the value obtained by Brauner in both his researches, but is over three-tenths of a unit higher than the choice of the International Committee upon Atomic Weights.

We are indebted particularly to the Carnegie Institution of Washington for pecuniary assistance in carrying out this investigation, and also to the Cyrus M. Warren Fund for Research in Harvard University for indispensable platinum vessels, as well as to Dr. H. S. Miner of the Welsbach Light Company for the praseodymium material.

CAMBRIDGE, MASS.

RECENT WORK IN INORGANIC CHEMISTRY.

By JAS. LEWIS HOWE.

Received January 25, 1915.

It might seem too soon for publication of chemical research to feel the effects of the war, especially as nearly half of the period that has elapsed since the outbreak of hostilities covered the summer vacation in the continental universities, yet that there has already been a decided influence is apparent in the fact that the *Zentralblatt* from August 9 to December 9 contains only 964 pages as against 1548 pages for the similar dates in 1913. A far more serious diminution of research is to be expected, when we realize that such a large proportion of the students of European and Colonial universities are "with the colors."

There is little that is particularly striking to chronicle in the progress of inorganic chemistry in 1914. The only radical departure from well-established ideas is found in variations in the atomic weight of lead from different sources. The theoretical considerations are discussed by Fajans¹

¹ *Physikal. Ztsch.*, 14, 951, and *Sitzber. Heidelb. Akad. Wiss., Math-naturw. Kl.*, 1914, 11, Abh. 22.

according to which it appears that the end product of decomposition in the uranium-radium series, Ra G, must be lead, but that it would have an atomic weight of 206.0, instead of 207.1, the atomic weight of ordinary lead. Similarly, the end products of the other radioactive series would have atomic weights varying from 206 to 210, that of the end-product of the Ra C₂ series. The first case has been studied by Richards¹ by determining the atomic weight of lead from different sources. While for ordinary lead from commercial acetate and nitrate the figure 207.15 was found, using the same methods of analysis the atomic weight of lead from English pitchblende was found to be 206.86 and from Joachimsthal pitchblende 206.57. Almost this same figure was found for Colorado carnotite, while uraninite from North Carolina gave a still lower value, 206.40. In general, the greater the radioactivity of the mineral, the lower the atomic weight of the contained lead. This variation is also confirmed by Maurice Curie² who finds the figure for lead in carnotite 206.36, in pitchblende 206.64, in yttriotantalite 206.54, but that in monazite was 207.08. From these results there would seem little doubt but that in lead there is a variable atomic weight, depending on its origin, and further work along this line will be awaited with interest.

Among the more general papers of the year is one by Kullgren³ on the hydrolysis of inorganic salts. Using the inversion method, the hydrolysis of a large series of salts, chiefly chlorides and nitrates of bivalent metals, was determined at 85.5° and 100°. In most cases the hydrolysis proceeds according to the equation: $\text{RCl}_2 + \text{HOH} = \text{R} \begin{smallmatrix} \text{OH} \\ \text{Cl} \end{smallmatrix} + \text{HCl}$, the value being the same for chlorides and nitrates, (except ZnCl_2). The reaction with aluminum salts appears to be with two molecules of water: $\text{AlCl}_3 + 2\text{HOH} = \text{Al} \begin{smallmatrix} (\text{OH})_2 \\ \text{Cl} \end{smallmatrix} + 2\text{HCl}$. (Lind has found by conductivity methods the hydrolysis of trivalent ruthenium also to be two-thirds.) In these salts with moderate hydrolysis the hydrolysis-constant is seldom a real constant. The hydrolysis of HgCl_2 (1.33) and PbCl_2 (1.49) is almost independent of dilution, but in the other salts there was some increase of hydrolysis. The degree of hydrolysis is decreased by the presence of neutral salts and this action is independent of the temperature. In a study of organic compounds of tin, Pfeiffer⁴ obtained the first hydrolytic product of stannic chloride and of stannic bromide, $\text{SnCl}_3(\text{OH}) \cdot 3\text{H}_2\text{O}$ and $\text{SnBr}_3(\text{OH}) \cdot 3\text{H}_2\text{O}$, by extracting a not too dilute aqueous solution of the halide with ether and recrystallizing the product obtained from water. From his work he draws the conclusion that these hydrates, as well as $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and $\text{SnBr}_4 \cdot 4\text{H}_2\text{O}$, are not aquo-salts, but simply addition compounds (Anlagerungsverbindungen). The coördination number of the tin atom is 6, two of the coördination positions being occupied by water. The structure thus becomes $[\text{Cl}_4\text{Sn}(\cdot\text{OH}_2)_2] + 3\text{H}_2\text{O}$, etc.

Cryoscopic measurements in nonaqueous solutions is a subject of great interest and slow development. Isbekow⁵ has worked with AlBr_3 as a

¹ THIS JOURNAL, 36, 1329 (1914).

² *Compt. rend.*, 158, 1676.

³ *Z. physik. Chem.*, 85, 466.

⁴ *Z. anorg. Chem.*, 87, 235.

⁵ *Ibid.*, 84, 24.

solvent, and finds that in this medium such substances as AlCl_3 , AlI_3 , CBr_4 and S , which give non-conducting solutions, have normal molecular weights. On the other hand HgBr_2 , SbBr_3 , BiBr_3 , CdBr_2 , PBr_3 and ZnBr_2 , whose solutions are electrolytes, are polymerized, the first three increasing in polymerization with the concentration. It appears as if in these cases the salt forms a complex ion with the solvent, which decomposes with increasing dilution into the simple undissociated molecule. Olivari¹ has used iodine as a solvent and worked chiefly with organic compounds, which at great dilution show normal molecular weights, but which associate with increasing concentration. The associating tendency is least with hydrocarbons and increases with the presence of hydroxyl groups. In concentrated solutions the molecule of sulfur is S_8 , but lower values are obtained on dilution. Selenium gives values between Se and Se_2 , the latter only in concentrated solutions. With tellurium, compounds are formed, as is evidenced by the evolution of heat, which seem to have simple molecules of the formula TeI_x . Iodides of the alkalis and organic iodides give abnormal results, the molecular weight increasing with concentration to a maximum value and then decreasing.

The action of ultraviolet light on metals has been investigated by Kimura.² He finds that when metals are covered with a layer of water or alcohol and exposed to ultraviolet light they are corroded and the material removed goes into solution in a colloidal form. The colloidal particles seem to consist of both metal and hydroxide. An alloy of 90% cadmium and 10% antimony showed no corrosion in vacuum but was acted on in the air, and much more strongly in pure oxygen. Kimura concludes that the action in air is due to the formation of ozone by the influence of the ultraviolet light. Under water, where the corrosion is much greater, hydrogen peroxide is in part the active agent, but not the exclusive one, as was shown by experiments on the action of hydrogen peroxide on silver.

From experiments at Kilauea in 1912, Brun concluded that in the gases of this volcano there was no water to which a magmatic origin could be attributed. More recent observations by Day and Shepherd³ indicate the reasons why Brun failed to detect this water, and show its presence. The gases were drawn by Day and Shepherd by means of a metal tube inserted in a narrow lava crack from direct contact with molten lava. Considerable quantities of water were obtained, which could only have been of magmatic origin. The gases, chiefly SO_2 and CO_2 , with a little CO , contained nitrogen, but no argon, as would have been the case had any atmospheric gases been present. The water collected was milky from precipitated sulfur, but contained neither chlorine nor titanium. These results are analogous with those of other observers on the gases of Mount Etna, except that here, as well as at Vesuvius, Stromboli and Santorin, large amounts of chlorine are present. It must be concluded that magmatic water plays a large role in volcanic eruptions, as has been generally believed.

The work of Ephraim⁴ on "Nebenvalenz," which was described last year, has been extended to the addition compounds of the halides of the

¹ *Atti accad. Lincei, Rome* [5] 22, ii, 697; 23, i, 41.

² *Mem. Coll. Sci. Engin., Kyoto*, 5, 253.

³ *Compt. rend.*, 157, 958, 1027.

⁴ *Ber.*, 46, 3742.

bivalent metals with substituted ammonias. Many of the addition compounds formed are analogous to those formed with ammonia, while others differ. The influence of the atomic volume of the central metal upon the affinity of the compound is clear, and in the case of Ni, Co, Fe, and Mn, the expression $\sqrt[3]{v} \cdot \sqrt[3]{T}$ (v = atomic volume of the metal, T = dissociation temperature) is nearly a constant, as was found to be the case in the addition products with ammonia. The affinity is also strongly affected both by the anion and also by the neutral portion of the molecule, but the irregularities are so far too great for much generalization. Pfeiffer,¹ working with the stannic halides, finds tin tetrachloride to possess the greatest affinity in the formation of addition products with ethers, esters, and nitriles. The addition compounds of the tetrabromide are far less stable, and no addition compounds were formed with any of the esters tested. If one chlorine atom in the tetrachloride is replaced by the methyl group, the affinity for esters, etc., almost ceases, while the substituted bromide forms no such addition products. All three tetrahalides form addition products with alkali salts and related compounds, as do the mono- and di-alkyl halides, but this is no longer the case with the stannic halides in which three or four of the halogen atoms are replaced by alkyl groups. The same is true regarding the tendency to unite with pyridine, but with ammonia the trialkyl derivatives, R_3SnX , form addition compounds, though this is not the case with the tetraalkyl compounds. Pfeiffer concludes that the affinity of the "Nebenvalenz" of tin decreases from chloride to bromide, and from bromide to iodide, and also decreases as the halogen atoms are progressively replaced by alkyl or phenyl groups. This is in general accord with the work of Ephraim.

Werner has continued his work² with rather striking results, especially in two particulars. First, in his study of the asymmetrical cobalt atom, he has prepared compounds with two cobalt atoms in the nucleus, to each of which are attached two ethylenediamine groups, and which are linked together by a NH_2 and a NO_2 group; these latter groups are held, half by primary and half by secondary valence. Such a compound ought to be capable of existing, like the analogous tartaric acid with two asymmetrical carbon atoms, in four forms, dextro and levo, racemic, and also the meso, or internally compensated inactive form. All of these forms were actually prepared by Werner in the series: $[en_2 Co \overset{NH_2}{\underset{NO_2}{\text{---}}} Co en_2]X_4$. The inactive forms were resolved into the dextro and levo forms by means of the active bromocamphorsulfonates, and the mixture of these two active forms gave again the inactive racemic form, which could be again resolved into the active forms. On heating with water the active forms become inactive, passing over into the meso forms which cannot be resolved into active isomers by the bromocamphorsulfonate. The meso salts are less soluble than the corresponding racemic salts, 100 parts of water dissolving 1.95 parts of the meso-bromide and 2.31 of the racemic bromide, 2.44 of the meso-iodide and 3.75 of the racemic iodide. From the optical behavior of the salts it appears that here there can be no difference between primary and secondary valence. Further work was done by Werner on similar compounds where the two cobalt atoms in the nucleus are linked together by

¹ *Z. anorg. Chem.*, **87**, 335.

² *Ber.*, **46**, 3674; **47**, 1954, 1961, 2171, 3087.

O₂ instead of NO₂, one of the cobalt atoms being quadrivalent. Here there should be four active forms and two racemic, several of which were obtained. These compounds are characterized by an extraordinary large rotation (in the bromide $[\alpha] = \pm 840^\circ$). Much more striking is the last piece of work which has come from the Zürich laboratory, an optically active substance which contains no carbon, and which has a rotation $[\alpha]_{560} = \pm 4500^\circ$, with a most extraordinary anomalous rotation-dispersion. The value of $[\alpha]$, for example, for wave-length 643.5 = -2100° for 617.0 = 0° , for 560 = $+4446^\circ$, for 495 = 0° , and for 478 = -858° . This compound belongs to the type (Co en)₃X_n, the place of ethylenediamine being taken by $\begin{smallmatrix} \text{HO} \\ | \\ \text{HO} \end{smallmatrix} \text{Co}(\text{NH}_3)_4$, the compound thus being

$[\text{Co}(\begin{smallmatrix} \text{HO} \\ | \\ \text{HO} \end{smallmatrix} \text{Co}(\text{NH}_3)_4)_3]\text{X}_6$, a dodekammine-hexol-tetracobalti-salt. The inactive form has been known for some time, and is prepared from the chloro-aquo-tetrammine-cobalt chloride by the action of dilute ammonia, with fairly good yield. The resolution into the active constituents is accomplished by the bromocamphorsulfonate method. Using the strychnine method Werner has resolved the rhodium oxalates into optical isomers, and here he finds anomalous rotation-dispersion, the potassium salt of the dextro acid having values of $[\alpha]_c = -26.4^\circ$, $[\alpha]_D = 0^\circ$, and $[\alpha]_B = +114.4^\circ$. He also finds that some racemic forms of cobalt compounds can be split into the active forms by crystallization, the solution being inoculated by traces of the active form, and this in some cases at least not necessarily of the same compound.

Both Ramberg¹ and Tschugajew² have continued their work on the complex compounds of platinum with the organic thio-compounds, the former using ethyl- and ethylene-thio-glycolic acid and obtaining both *cis*- and *trans*-isomers. In working with the thiobases, Tschugajew found much difficulty in determining the composition of the complex kation, owing to the tendency to form salts of the Magnus type, platinum being thus present in both kation and anion. He has now found that these salts can be resolved by salts of several acids, as nitroprussides, chlororhodates, phosphotungstates, but, best of all, by picrates, and he recommends picric acid as a valuable reagent for complex kations. He has also prepared a number of complex platinum salts with hydrazine and with both hydrazine and ammonia. In these the hydrazine acts like the ammonia and occupies only a single coördination-position. In addition to the large number of complex salts of the metals of the platinum group which he has already described, Gutbier has now studied the bromoplatinates,³ the bromoaurates,⁴ and the chloro- and bromo-tellurates.⁵ Large numbers of salts of each of these classes have been prepared, both with inorganic and organic bases, and are fully described. In the balance of this review the order of the periodic table will be followed.

Group II.—K. A. Hofmann⁶ has found fused anhydrous magnesium chloride an excellent solvent for many inorganic oxides, and from the melt

¹ Ber., 46, 3886; 47, 730.

² Z. anorg. Chem., 86, 241; Ber., 47, 2446.

³ J. prakt. Chem., [2] 88, 409; Sitzber. physik.-med. Soz., Erlangen, 45, 25.

⁴ Z. anorg. Chem., 85, 353.

⁵ Ibid., 86, 169.

⁶ Ber., 47, 238.

fine crystals are generally obtained. The oxides may be directly dissolved, or other compounds used, especially the sulfates, which undergo decomposition in the melt. The magnesium oxide which is always present in the crystallized mass may be removed by acetic acid or dilute hydrochloric acid. By using iron filings, or dehydrated ferrous sulfate, or Fe_2O_3 , and varying the time of fusion, $\text{Mg}(\text{FeO}_2)_2$, $\text{Fe}(\text{FeO}_2)_2$, or the intermediate magnesio-ferrites, are obtained. Fine crystals of magnesium borate, $3\text{MgO} \cdot \text{B}_2\text{O}_3$, are formed in the melt of MgCl_2 with boric acid, and $3\text{MgO} \cdot \text{U}_2\text{O}_6$ when uranic oxide is used. CeO_2 can be obtained in brilliant crystals of extreme hardness, by the use of cerium sulfate. These crystals are colorless, but if small quantities of rare earth sulfates (Er, Nd, Pr) are added to the fusion beautifully colored crystals are formed. ZrO_2 may be similarly obtained. From the fusion with erbium, neodymium, praseodymium, and samarium-sulfates, the oxychlorides are gotten, ErOCl , NeOCl , PrOCl , SmOCl , and these show in reflected arc light the characteristic spectra of the metals. This method is suggested as a useful one in the investigation of these, and possibly other rare earths. Hedvall¹ has extended his study of Rinman's Green, which proved to be a solid solution of the components, to the red produced by heating magnesium oxide with cobalt compounds. The two oxides were heated directly with a potassium chloride flux, at temperatures from 1100° to 1400° . Crystals were formed which varied under the microscope from colorless to ruby-red, and which were octahedra, often with cube faces. While it was not possible to follow the homogeneity of the crystals through the whole series, for a considerable interval—38–79% CoO —they could be shown to be homogeneous, and it seems probable that a complete miscibility subsists between MgO and CoO in all proportions. The specific volume of the products decreases continuously with increasing content of CoO .

Group III.—The work of Stock on the borides of hydrogen, which was described in the review of last year, has been extended to the reactions of these borides on the alkalis² and on the halogens.³ For action with the alkalis H_{10}B_4 was chosen, since H_6B_2 is so sensitive to the presence of moisture. With both the borides, however, the same product is formed and hydrogen is evolved, molecule for molecule. The reaction is: $\text{H}_{10}\text{B}_4 + 4\text{KOH} = 4\text{KOBH}_3 + \text{H}_2$. The salt formed, potassium hypoborate, is stable in the absence of moisture, and at 0° its solution can be preserved for several hours without decomposition. At ordinary temperature the solution decomposes with evolution of hydrogen and formation of KBO_2 : $\text{KOBH}_3 + \text{H}_2\text{O} = \text{KBO}_2 + 5\text{H}$. The solution gives an alkaline reaction, owing to hydrolysis. It is a powerful reducing agent, resembling in this respect the hypophosphites, which it also resembles in structure. Solutions of aluminum, zinc, manganese, and the alkaline earths are precipitated, hydroxides and borates being formed, while in solutions of silver, bismuth, mercury, arsenic, and antimony, a dark precipitate of the free metal appears at once. In copper solutions copper hydride is formed. The most characteristic reaction is that with nickel solutions, in which black, insoluble nickel boride, Ni_2B , is precipitated; in dry condition this is so easily oxidized that it ignites spontaneously. In a vacuum at 500°

¹ *Z. anorg. Chem.* **86**, 296.

² *Ber.*, **47**, 810.

³ *Ibid.*, 3113, 3115.

potassium hypoborate loses $\frac{2}{5}$ of its potassium, which distils off, while hydrogen is also evolved, and a residue with the formula $K_3B_5O_8$ remains, which is probably not a definite compound. In both potassium hypoborate and the nickel boride, the boron is evidently quadrivalent. For reaction with the halogens H_2B_2 was chosen, as being the simplest of the borides of hydrogen. When an excess of chlorine or bromine is used, the resultant product is BCl_3 or BBr_3 , but, by using smaller proportions of the halogen, evidence of the formation of intermediate compounds was obtained, and B_2H_5Br was isolated. B_2H_5Cl is probably a spontaneously inflammable gas. It seems also probable that $B_2H_4X_2$ and $B_2H_3X_3$ may exist, but break up into B_2H_6 , B_2H_5X , and BX_3 . No evidence could be found for the existence of any of the partially halogenated compounds with a monomolecular formula, as BH_2X or BHX_2 ; nor do any more highly halogenated compounds, such as $B_2H_2X_4$ or B_2HX_5 , appear capable of existence. Further, neither BCl_3 nor BBr_3 will take on more of the halogen. While these results which Stock has obtained in boron compounds are altogether unexpected, yet they are not really anomalous. Theoretically, the maximum positive valence of boron is three, and this has not been exceeded in any of these compounds. The maximum negative valence is five, and in the hydrogen borides of Stock it reaches four, and the compounds appear to have similar constitutions to some of the compounds of carbon and hydrogen, as H_2B_2 and $H_{10}B_4$, boroethane and borobutane. In boroethane the hydrogen is replaceable by halogens, as in ethane; when fully replaced, the boron being now positive to the chlorine, or bromine, the B_2Cl_6 spontaneously breaks down into 2 BCl_3 .

The compounds of boric acid with thallium have been studied by Buchtala.¹ No compounds with trivalent thallium could be obtained, but the thallous borates are formed by solution or fusion of thallous carbonate or hydroxide with boric acid. The series from $Tl_2O \cdot B_2O_3$ to $Tl_2O \cdot 6B_2O_3$, with varying quantities of water, was prepared, and the members resemble the borates of the alkalis except in their water content. All these thallous borates give with hydrogen peroxide a perborate, with formula $Tl_2B_2O_7$, which decomposes explosively on heating, and on warming with water evolves three atoms of oxygen. To this perborate Buchtala

assigns the constitution

$$\begin{array}{c} \text{OTl} \\ | \\ \text{B} \begin{array}{l} \diagup \text{OTl} \\ \diagdown \text{O} \end{array} \\ | \\ \text{O} \diagup \text{O} \diagdown \\ | \quad \quad | \\ \text{O} \diagup \text{O} \diagdown \\ | \\ \text{B} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OTl} \end{array} \end{array}$$

though it is difficult to see why he

should consider the two boron atoms to be linked together.

The fourth paper of R. J. Meyer² on scandium presents several points of interest. The most characteristic distinctions between scandium and the other "earths" depend upon its more negative character. From this follows the strong tendency of its salts to hydrolysis, and also to form complex ions. In its hydrolytic tendency scandium resembles aluminum; its chlorides and nitrates in solution are weakly acid, and when heated are partially precipitated by sodium acetate, and completely by sodium

¹ *J. prakt. Chem.*, [2] 88, 771.

² *Z. anorg. Chem.*, 86, 257.

thiosulfate. The solution of the sulfate is only incompletely precipitated, owing to the formation of complex salts. In this tendency to form complex ions scandium resembles zirconium and thorium, indeed, in many respects it stands chemically quite close in its properties to thorium. It is distinguished from aluminum by not being amphoteric. Double chlorides of scandium and the alkalis could be realized only in the case of cesium, as seems to be the case also with several of the rare earth metals. Double fluorides are, however, formed, as K_3ScF_6 . Scandium sulfate is the scandium salt of a scandium-sulfuric acid, $H_3(Sc(SO_4)_3)$, of which also the alkali salts, as $K_3(Sc(SO_4)_3)$, were prepared. This constitution is confirmed by the work of Wirth,¹ who by dissolving scandium sulfate in sulfuric acid obtains white crystals of the formula $Sc_2(SO_4)_3 \cdot 3H_2SO_4$, which is in reality the above-mentioned scandium-sulfuric acid. Wirth also finds that when scandium sulfate is heated in dry H_2S the sulfide Sc_2S_3 is formed, which is fairly stable in dry air. Among the other salts investigated by Meyer are the oxalates, and here also, like thorium, scandium forms complex anions. The complex oxalates of the formula $R'Sc(C_2O_4)_2$, are very stable and only slowly decomposed, even by sulfuric acid. These oxalates have also been studied by Wirth, who has prepared salts of the scandium-oxalic acid, $H_3(Sc(C_2O_4)_3)$, and it appears that scandium oxalate itself, $Sc_2(C_2O_4)_3 \cdot 5H_2O$, is in reality the scandium salt of this acid. Among other recent workers on scandium is Lukens,² who has separated it from the residues of Colorado wolframite, and determined its atomic weight from the sulfate-oxide ratio; and Sterba-Böhm,³ who has purified scandium by the fractionation of the formate. From this work the latter concludes that scandium is a simple element. He has also investigated the rose-colored sulfide supposed by Ogawa to contain a new element, and finds that it consists exclusively of sulfur and copper sulfide.

Group IV.—Lely and Hamburger⁴ have prepared metallic titanium, zirconium, thorium and uranium in a state of very considerable purity (uranium 99.5% pure) by the reduction of the chlorides by metallic sodium. The anhydrous chlorides were in general formed by the action of carbon tetrachloride or the chloride of sulfur in a chlorine atmosphere. Metallic titanium is less ductile than the other metals and the pulverulent metal can be formed into coherent masses only with great difficulty. It is also much less resistant to reagents. Zirconium was obtained in large metallic leaflets and easily gave a metallic mirror by rubbing in an agate mortar. While more easily oxidized than titanium, it is much more resistant to acids and alkalis, though readily attacked by hot *aqua regia* or oil of vitriol. Hydrofluoric acid, even when dilute, attacks it rapidly in the cold. Metallic thorium is lead-gray, and very stable in the air, as well as toward alkalis in solution and nitric acid. In hydrochloric acid hydrogen is evolved, but the metal does not dissolve completely. By *aqua regia* thorium is oxidized to ThO_2 . Metallic uranium is darker than thorium, but quickly colors brown in the air. It is not attacked by water or alkaline solutions, nor by acetic acid. In dilute hydrochloric acid hy-

¹ *Z. anorg. Chem.*, **87**, 1, 7, 9.

² *THIS JOURNAL*, **35**, 1470.

³ *Z. Elektrochem.*, **20**, 289.

⁴ *Z. anorg. Chem.*, **87**, 209.

drogen is evolved and UCl_4 formed, but in the concentrated acid the metal quickly dissolves to a violet-colored solution of UCl_3 , which, however, slowly goes over into green UCl_4 . The metal dissolves rapidly in nitric acid with the formation of uranyl nitrate.

Group V.—The question of the existence of an active form of nitrogen has continued to attract the attention of several chemists during the past year. Strutt first called attention to the orange-yellow cloud-like luminescence observed when the electric discharge is passed through nitrogen at pressures from 1 to 10 mm., and ascribed it to an active modification of the nitrogen. In this gas many elements and compounds are acted on with the formation of nitrogen compounds. This was first contested by Comte, who claimed that the luminescence was due to the presence of traces of oxygen, and the compounds to a nitrogen oxide. Tiede and Domcke¹ have repeated a second time Strutt's experiments, using every precaution to free the nitrogen from traces of oxygen and to avoid any possible access of this gas. By adding traces of oxygen the luminescence appeared, by its withdrawal the luminescence was reduced to a minimum. If too much oxygen is added the luminescence disappears. From this the conclusion is drawn that so far from being a proof of the existence of active nitrogen, the luminescence is a sensitive reagent for traces of oxygen in nitrogen. Fischer² agrees with Tiede, and ascribes the phenomena to the activation of the traces of oxygen rather than to the nitrogen. These conclusions are disputed by Koenig and Elöd,³ by Baker and Strutt,⁴ by Strutt⁵ and by de Kowalski.⁶ According to the first, the luminescence is to be looked upon as an accompaniment of active nitrogen, not as proof of its existence. This is proved by its reactions at ordinary temperatures with substances which do not react with nitrogen in its common form. Among many other substances, pentane, carefully purified from all unsaturated hydrocarbons, reacts with active nitrogen, giving amylene, ammonia and a trace of hydrogen cyanide. Not only nitrogen is capable of being thus activated, but pure oxygen gives a modification more active than ozone and this phenomenon is also accompanied with luminescence. Since metallic vapors destroy or inhibit the luminescence of nitrogen, the failure of Tiede to obtain luminescence in his pure nitrogen is attributed to the presence of mercury vapor, or of the metals from the azides which he used to furnish his nitrogen. de Kowalski also obtains the luminescence in nitrogen enclosed in a glass globe in an induced electric field. The work of the others is all confirmatory of the original work of Strutt, but the large volume of exceedingly interesting experimental work must be passed over in this review, which has aimed to touch on only the most salient points.

An apparently successful attempt to solve the problems which surround the conditions of existence of nitrogen sesquioxide has been made by Klinger.⁷ He finds that dry N_2O_3 is rapidly and quantitatively absorbed

¹ *Ber.*, 46, 4095; 47, 420.

² *Ibid.*, 46, 4103.

³ *Ibid.*, 47, 516, 523.

⁴ *Ibid.*, 801, 1049.

⁵ *Physik. Ztsch.*, 15, 274.

⁶ *Compt. rend.*, 158, 625.

⁷ *Z. angew. Chem.*, 27, 7.

by dry caustic potash. Enclosing sticks of dry caustic potash in a measured excess of dry oxygen, in a pipet, he added a measured quantity of NO. The diminution of volume was $\frac{5}{4}$ that of the NO added, corresponding to the equation: $4\text{NO} + \text{O}_2 = 2\text{N}_2\text{O}_3$. Had NO_2 been formed, the diminution would have been $\frac{3}{2}$ corresponding to: $2\text{NO} + \text{O}_2 = 2\text{NO}_2$. From this the conclusion is drawn that oxygen does not unite directly with NO to form NO_2 , but that N_2O_3 is formed as an intermediate product. Again, NO_2 is instantly absorbed by caustic potash to a mixture of nitrite and nitrate, while NO does not form any compound instantaneously. A mixture of equal molecules of NO and NO_2 was immediately and completely absorbed by caustic potash with the formation of potassium nitrite, consequently no NO or NO_2 , as such, could have been present, or some of the NO would have been left over, and some nitrate formed. It follows that a mixture of NO and NO_2 must be looked on as N_2O_3 .¹ Several years ago Raschig described a new oxide of nitrogen formed by leading NO into liquid air, and ascribed to it the formula NO_3 . This has been disputed by Müller, and Raschig has repeated and extended his work.² The compound is also formed, as noted by Müller, by a high-tension electric flame in liquid air, and is a light green precipitate, becoming a dull gray-blue as the oxygen evaporates. The compound cannot be N_2O_3 , as was contended by Müller, since this is deep indigo-blue, both in solid and in liquid form. On the evaporation of the liquid air there is left at -110° a dull blue solid, which breaks up at -100° , and which has the formula NO_2 . Since it possesses none of the ordinary properties of NO_2 or N_2O_4 , it must be an isomer, and Raschig calls it iso-nitrogen tetroxide. The dull green compound from which the iso-tetroxide is formed, after washing with liquid nitrogen is nitrogen hexoxide, NO_3 . Raschig's work is again criticized by Müller,³ who claims that the supposed NO_3 is merely a mixture of NO_2 , N_2O_4 , N_2O_3 and NO, and that on washing with liquid nitrogen it loses no oxygen, and no iso-tetroxide is formed. Mention should be made of a very complete investigation of nitrites, their conditions of formation and decomposition, by Oswald,⁴ which however, does not admit of useful abstraction. Ball⁵ has continued his study of bismuth nitrites, and prepared a large number of new salts, in which the tendency of bismuth to form triple nitrites is very apparent. Of the fifteen possible salts of the formula $\text{X}_2\text{YBi}(\text{NO}_2)_6$, where $\text{X} = \text{NH}_4$, K, Rb, Cs, Ti^+ , and $\text{Y} = \text{Li}$, Na, Ag, all were prepared. Of triple nitrites with nickel, $\text{K}_4\text{NiBi}_3(\text{NO}_2)_{12}\cdot\text{aq.}$ and the corresponding thallium salt (anhydrous), were obtained, and also $\text{Rb}_7\text{NiBi}_3(\text{NO}_2)_{18}\cdot 4\text{H}_2\text{O}$ and the corresponding cesium salt with 6 H_2O . There would seem to be still considerable field for investigation among the curious triple nitrites, which, except by Ball, has hardly been touched since the work of Przibylla on the triple nitrites of nickel. In his work upon the compounds of nitric oxide on salts of iron and copper, Manchot⁶ has, for the first time, prepared

¹ The density of the mixture demonstrates that at ordinary temperature N_2O_3 dissociates almost completely into NO and NO_2 . —EDITOR.

² *Z. anorg. Chem.*, **84**, 115.

³ *Ibid.*, **86**, 230.

⁴ *Ann. chim. phys.*, [9] **1**, 32.

⁵ *J. Chem. Soc.*, **103**, 2110.

⁶ *Ber.*, **47**, 1601, 1614.

a ferrous-nitric oxide compound of the brown series in a solid crystallized condition. A solution of ferrous chloride in alcohol was saturated with NO and kept in an NO atmosphere. This was precipitated with an alcoholic solution of di-ammonium hydrogen phosphate, a thick oil separating out, which became crystalline at -15° . The compound is $(\text{FeNO})\cdot\text{HPO}_4$, is fairly stable, fuses at $+16^{\circ}$, and in it there is present one molecule of NO to each Fe atom. It is oxidized rather slowly in the air or when shaken in water, gradually losing its very dark brown color and becoming white; in concentrated sulfuric acid it dissolves to a deep red solution. Similar salts are obtained with other inorganic acids, but not with organic. Thus, while oxalic acid gives with ferrous solutions an insoluble ferrous oxalate, if the solution is saturated with nitric oxide there is no precipitate, the ferrous-nitric oxide oxalate being very soluble. In these compounds there is present the bivalent kation $(\text{FeNO})^{++}$. The reaction of cupric chloride and bromide with nitric oxide does not seem to be characteristic of bivalent copper in general, since there was found to be no absorption of nitric oxide in solutions of the fluoride, nitrate, acetate, formate, amidoacetate, and other cupric salts in absolute alcohol. The NO in $\text{CuBr}_2\cdot\text{NO}$ is so sensitive to the presence of water that it would seem that there is a competition between the H_2O and NO molecule for the available addition-position. The action of nitrogen and hydrogen on the alkaline earth metals has been studied by Dafert and Miklauz,¹ the strontium and barium being obtained by distilling a mixture of the oxide with aluminum in a vacuum, and the calcium by redistilling commercial calcium. Metallic calcium begins to react with nitrogen at about 400° , while strontium reacts somewhat lower and barium at 260° . In each case the nitride M_3N_2 is formed. These nitrides begin to absorb hydrogen at 230° – 300° ,—calcium at the lowest temperature—with the formation of a trimetalamide, $\text{M}_3\text{N}_2\text{H}_4$. In the case of calcium an intermediate product is formed, which is probably tricalciumimide, $\text{Ca}_3\text{N}_2\text{H}_2$, which is especially sensitive to the light. Barium nitride on absorbing hydrogen gives off nitrogen, partly as ammonia. The substance produced is scarcely sensitive to light, and is of interest because at 700 – 750° it absorbs nitrogen with evolution of hydrogen, and then at 300 – 400° in a current of hydrogen gives off the nitrogen again, partly as ammonia. These reactions present possibilities of being utilized for the commercial production of ammonia from nitrogen and hydrogen. Calcium reacts with hydrogen at 300° , with strontium the reaction begins at 215° , and with barium at 120° . In each case the hydride, MH_2 is formed. Somewhat below a red heat these hydrides absorb nitrogen, the first two giving the imides CaNH and SrNH , but with barium hydride no imide is formed. At higher temperatures nitrides are obtained. A relatively pure calcium imide, which is very sensitive to light, is formed by heating calcium hydride, or better, calcium nitride to 730 – 750° in a stream of equal parts hydrogen and nitrogen.

In the course of a paper on the characteristics of the different modifications of phosphorus² Stock and Stamm consider the question as to whether the vapors of yellow and red phosphorus are identical. Red phosphorus, distilled from the hot to the cold end of an evacuated tube at 280 – 400° , condenses always in small part to red phosphorus again,

¹ *Monatsh. Chem.*, **34**, 1685.

² *Ber.*, **46**, 3497.

while both the yellow phosphorus and the Hittorf modification give colorless distillates. From this and other experiments, it is concluded that in vapor from red phosphorus there are actually present red phosphorus molecules, but that their concentration is exceedingly small. The chief constituent of the vapor of phosphorus of any kind is P_4 , which dissociates to a slight extent,—10.5% at 900° and 120 mm.—into P_2 . The equilibrium: $P_4 \rightleftharpoons 2P_2$ is displaced by decreasing pressure and increasing temperature in favor of P_2 ; the equilibrium: $xP_2 + yP_4 \rightleftharpoons P_{2x+4y}$ (red phosphorus vapor) is by decreasing pressure and increasing temperature displaced against the red phosphorus.

Group VI.—An investigation of the polysulfides of sodium was carried out by Rule and Thomas¹ in absolute alcohol. Metallic sodium was dissolved in alcohol and then saturated with H_2S and the excess of gas removed by a stream of hydrogen, while the solution was on a water bath. In this solution of $NaSH$, aliquot atomic quantities of sulfur were dissolved, and the solid product obtained by evaporation, or cooling, or both. The only pure compound which could be obtained was the tetrasulfide, Na_2S_4 . There was evidence of the existence of a higher polysulfide, but none could be isolated. The tetrasulfide is therefore to be looked on as the chief product of the action of sulfur on sodium hydrosulfide in alcoholic solution. By the action of metallic sodium the tetrasulfide is reduced (in alcohol) to the disulfide, Na_2S_2 , which is obtained as a microcrystalline powder, while sodium hydrosulfide remains in solution. It has long been a puzzle why nickel and cobalt sulfides, which are not soluble in acids, should not be precipitated from acid solutions by hydrogen sulfides. Two explanations have been offered: (1) The sulfides are insoluble, but their non-precipitation in acid solutions is due to a persistent supersaturation; (2) the sulfides are primarily precipitated in a form soluble in acids, which rapidly passes over into an insoluble form ("by polymerization"). Two other complications offer themselves, in that on long standing hydrogen sulfide does sometimes precipitate nickel sulfide, and the precipitated sulfides are generally, especially when freshly precipitated, far from completely insoluble in hydrochloric acid. The problem in regard to nickel sulfide has been attacked, with seeming success, by Thiel.² He finds that nickel sulfide when freshly precipitated is a mixture of three modifications, which he calls α , β , and γ , all of which have the formula NiS . αNiS is rapidly soluble in dilute HCl , but gradually passes over into the β and γ forms on standing, especially with access of air. It is predominately precipitated when dilute nickel solutions are slowly added to dilute alkali sulfide solutions in the cold and without access of air. In such cases it may be present in the precipitate to the extent of 85%. It is possible to wash it, dry it with alcohol, warm, and even heat it to red heat without its being completely converted into the other modifications. βNiS is very slightly soluble in cold HCl , but dissolves slowly in hot 2*N* acid. It is converted into γNiS by boiling several hours with 2*N* acetic acid. It is precipitated free from αNiS and with but little γNiS by H_2S from a hot solution of nickel acetate with excess of acetic acid. γNiS is insoluble in cold 2*N* HCl , and its solubility in the hot acid is very slight (0.0013 g. in 100 cc.). It remains as residue when a precipitated NiS

¹ *J. Chem. Soc.*, 105, 177.

² *Sitzber. med.-naturwiss. Ges. Münster*, 1913.

is extracted with hot HCl, in the form precipitated by H_2S after long standing from solutions not too strongly acidified with mineral acids, and into this the other forms are converted by boiling with acetic acid. β and γ forms are obtained when H_2S acts on nickel carbonate or hydroxide, and this explains the action of the air in converting the α modification into these forms; the air oxidizes the α NiS to the hydroxide and this is secondarily converted into the β and γ NiS by an excess of hydrogen sulfide. These changes seem clearly to be polymerization processes.

Several years ago Rosenheim prepared complex molybdenum cyanides with the formula $M_4'Mo(CN)_8$, the only known compound in which eight coördinated groups surround the central atom. In these compounds the molybdenum appeared to be quinquivalent, so that the compound does not seem to accord with the ordinary valence rules. He has now¹ prepared analogous tungsten cyanides which correspond in every way to those of molybdenum, and in which the tungsten, as determined by titration with $KMnO_4$, is also quinquivalent. The $(W(CN)_8)^{iv}$ group is even more stable than the ferrocyanide group, and the free acid can be prepared. Apparently independent of Rosenheim's work, Olsson² has prepared these same tungsten octocyanides, but he differs from Rosenheim regarding the valence of the tungsten atom, holding that it is quadrivalent, as would be expected. The results of the permanganate titration he explains by assuming that instead of being oxidized to WO_3 , the tungsten forms a complex in which its valence reaches only five. A fuller description is later given³ by Olsson, and he has succeeded in isolating the complex of quinquivalent tungsten, formed by oxidation with $KMnO_4$, and in preparing the series of salts $M_3'W(CN)_8$, in which the tungsten is quinquivalent.

Group VII.—As a method of preparing anhydrous chlorides, Conduché⁴ proposes heating sulfates, which have already been rendered anhydrous, in a current of dry carbon dioxide and chloroform. The reaction with $CuSO_4$ begins at 250° , with $NiSO_4$ and $FeSO_4$ at 300° , and with other sulfates at slightly higher temperatures, $BaSO_4$ and $CaSO_4$ reacting at 500° . At 280 – 300° by this method $CuCl_2$ is easily obtained in a pure and anhydrous condition. At a higher temperature $CuCl$ is also formed, the reducing action of the chloroform coming also into play. The chloroform acts like a mixture of chlorine and hydrogen chloride and different chlorides of the same metal may be formed at different temperatures. In the case of iron, whether one starts from ferrous or ferric sulfate, both ferrous and ferric chloride are obtained, and can be readily separated by the sublimation of the latter.

Group VIII.—Bellucci and Corelli have continued their efforts⁵ to isolate the double cyanide of univalent nickel, described last year. By the reduction of $K_2Ni(CN)_4$ solution with potassium amalgam in a hydrogen atmosphere, they obtain a dark red solution from which alcohol precipitates an exceedingly unstable, dark red, oily substance, which when dissolved in water gives the ratio $Ni : 3CN : 2K$, and which on titration

¹ *Ber.*, 47, 392.

² *Ibid.*, 917.

³ *Z. anorg. Chem.*, 88, 49.

⁴ *Compt. rend.*, 158, 1180.

⁵ *Atti accad. Lincei, Rome* [5] 22, ii, 485.

with iodine takes up one atom of iodine for each atom of nickel. This establishes the formula, as was expected, as $K_2Ni(CN)_3$, or $2KCN.NiCN$, the complex containing nickel in a univalent condition. Tschugejew and Chlopin¹ have also obtained univalent nickel by the reduction of nickel salts by a concentrated solution of sodium hydrosulfite and nitrite in equimolecular proportion. A violet or blue coloration is produced according to the amount of reagent used. The violet solution contains $HN(NiSO_3)(HSO_3).nH_2O$, which could not, however, be obtained in a completely pure condition. Sodium hydroxide gives a blue precipitate of what is apparently $NiOH$, but which could not be dried without decomposition. This is converted by sodium sulfide into black Ni_3S , which can be isolated only in moist condition. The blue hydrate dissolves in KCN to a red solution, which seems to be identical with that of Bellucci's $K_2Ni(CN)_3$.

Barbieri² has entered on a systematic study of resemblances between compounds of elements in different groups of the periodic system, when these elements have the same valence. Thus an element of the eighth group, acting with a valence of three, may be, for practical purposes, considered as an element of the third group. As examples he has prepared Ruthenium acetylacetonate, $Ru(C_5H_7O_2)_3$, and finds it to closely resemble aluminum acetylacetonate, with which it is isomorphous and gives solid solutions. Ammonium rhodio-molybdate, $3(NH_4)_2O.Rh_2O_3.12MoO_3.20H_2O$, is in every way similar to the corresponding Al , Fe''' , and Cr''' salts, as well as to the Co''' salt of Friedheim and Keller. The isomorphism of palladium acetylacetonate with the corresponding cupric salt was shown by the formation of solid solutions. Delépine³ has succeeded in preparing the very soluble chloro-iridates and iridites of lithium. Li_2IrCl_6 crystallizes as a hexahydrate, and when crystallized with sodium chloro-iridate does not form any intermediate compound. When reduced by alcohol $Li_3IrCl_6.12H_2O$ is formed and hydrogen chloro-iridite remains in the mother liquor. No intermediate lithium-hydrogen salt is formed. Better results are obtained by reducing the lithium chloro-iridate with lithium oxalate. By mixing with solutions of sodium chloro-iridite, the intermediate compounds, $Na_2LiIrCl_6.12H_2O$ and $Na_{1.1}Li_{1.9}IrCl_6.12H_2O$, were obtained, but when recrystallized from water the sodium salt resulted, containing very small quantities of lithium. Fraenkel has prepared⁴ a number of new salts of rhodium and iridium with organic bases. Chloro-iridic acid gave only the familiar type, $M_2' IrCl_6$. With rhodium, however, not only the type $M_3' RhCl_6$ was obtained, but also $M_2' RhCl_6$ (with methylamine), $M_4' RhCl_7$ (with methylamine and tetraethylamine), and $M_3' Rh_2Cl_9$ (with trimethylamine and tetraethylamine).

NOTE.

A Surface Burn Produced by an Unknown Radiation.—Woehler,⁵ in 1862, heated carbon and an alloy of calcium and zinc together and

¹ *Compt. rend.*, 159, 62.

² *Atti accad. Lincei, Rome* [5] 23, i, 334.

³ *Compt. rend.*, 158, 1276.

⁴ *Monatsh. Chem.*, 35, 119.

⁵ F. Woehler, "Bildung des Acetylens durch Kohlenstoffcalcium," *Ann. Chem. Pharm.*, 124, 220 (1862).

obtained a product which evolved acetylene when treated with water. He called the product calcium carbide.

The alloy had been previously described by Caron,¹ who got it by adding metallic sodium to fused calcium chloride in the presence of molten zinc. This alloy is of silvery luster, highly crystalline, and contains from 10% to 15% calcium.

On repeating Woehler's experiment, in connection with other experiments on making calcium carbide by different methods, use was made of a gas crucible furnace of present day type. The objection was raised that a temperature was thus secured higher than that Woehler probably worked with. Accordingly, an old-fashioned assay furnace of French clay, which had come to me as an heirloom, was set up. This furnace was in three sections, the lower one having a grate and ash pit, the second section being merely a ring, and the third, or top section being dome shaped, and having a central round opening on top which was connected to a wide chimney by means of a sheet iron smoke stack.

Caron alloy was made by melting lumps of fused C. P. calcium chloride and granulated zinc, 20 mesh, in a Dixon graphite crucible and adding slices of metallic sodium. The reaction is at times violent. The results on cooling a fine regulus of the calcium zinc alloy. Charcoal was used as fuel.

Separate portions of this alloy were made at different times and heated with different varieties of carbon, such as charcoal, coke, lampblack and gas carbon, a sample of the latter dating from 1850 to 1860 being found among apparatus left me.

On Nov. 30, 1907, two charges were run in the furnace. In the first, use was made of alloy and gas carbon, in the second alloy and lampblack. The operation was conducted with 1100 g. of a 14% alloy and 110 g. of lampblack, using a No. 6 Dixon crucible. It took three hours to distill off the zinc, during which time I sat with the furnace between my knees feeding in the charcoal used as fuel through a side opening in the stack. Though the work was somewhat dirty no inconvenience was felt at the time. Later on, undressing for a bath, the inner surface of each knee was found red, and there was a water blister, about 1 cc. in diameter, in the center of the red surface on the left knee. The red patch was about the size of my hand, that on the right knee half that size.

Since this effect had been produced not only through a pair of thick trousers but thick woolen drawers under them, without my noticing any sensation, and as the burn appeared like one made by X-rays, with which I was familiar, it was later shown to Drs. Robert Abbe and Henry G. Piffard, both of whom were familiar with X-ray and radium burns and they agreed with my diagnosis, and considered the burn was similar in character to burns produced by those agencies.

¹ H. Caron, *Compt. rend.*, 50, 547 (1860).

The nature of the burn was further confirmed by the fact that it took long to heal, traces of it were visible Mar. 31, 1908, or four months later.

To further test the theory, at Dr. Abbe's suggestion, the experiment was repeated on Dec. 21, and to eliminate the personal equation a sheet of lead, perforated with five holes, was interposed between the Cramer X-ray "X" plate, enclosed in the usual black and yellow papers, and the portion of the furnace corresponding to the height of my knee from the floor, while the zinc was distilled. There is a crack around the furnace at this point, and it was about there that the fumes of burning zinc could be seen within the furnace. Alloy and lampblack were again used in the charge. The plate was exposed for 1 hr. and 17 min. at a distance of 2 ft. from the furnace, and a thermometer placed beside the plate showed a temperature ranging from 25° to 35° , with one time a temperature of 42° .

The plate was given to a photographer to be developed along usual lines, but he was not told what might appear on the plate. The developed plate and a positive printed from it show the five holes in the lead covering plate and thus confirm the diagnosis of the nature of the burn.

Later, other plates were exposed during runs but no distinct effects produced. Nor was there any similar result to the first obtained when Messrs. Stone and Riggs kindly exposed similar plates behind the perforated lead plate to the light of burning zinc at the furnaces of the New Jersey Zinc Company.

Both the burn and the effect on the X-ray plate were produced when alloy and lampblack were used. When coke, charcoal, and gas carbon were used with the alloy no photographic evidence was obtained. The lampblack was purchased in open market, as also the zinc, calcium chloride, and sodium, the other chemicals used. The fuel was either ordinary charcoal or in the later experiments coke or coal or both together. The Dixon crucibles and covers were new.

As an opportunity has not presented itself for me to repeat these experiments methodically and determine the cause of the phenomena the facts are placed on record in the hope that sometime an explanation will be forthcoming.

CHARLES A. DOREMUS.

NEW YORK, N. Y.
December, 1914.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY.]

THE INFLUENCE OF TEMPERATURE IN ACID CATALYSIS.

By HUGH STOTT TAYLOR.

Received December 21, 1914.

Since the suggestion was put forward by Goldschmidt,¹ Snethlage²

¹ *Z. physik. Chem.*, **70**, 627 (1910); **81**, 30 (1912).

² *Z. Elektrochem.*, **18**, 539 (1912); *Z. physik. Chem.*, **85**, 211 (1913).

and Acree¹ that, in addition to the hydrogen ion, the undissociated molecule of an acid has a catalytic effect, interest in reactions catalyzed by acids has been markedly stimulated. Snethlage amplified the observation by calling attention to the fact that the stronger the acid, or the greater its dissociation constant, the more active was the undissociated molecule catalytically as compared with the hydrogen ion.

In a series of researches the author, acting upon the above suggestion, showed that the theory was quantitatively applicable, in addition to the catalytic reactions of acids in organic solvents as studied by the investigators cited above, to reactions in aqueous solutions. The first investigation² showed that neutral salt action in ester catalysis was independent of the ester substrat, that, therefore, the existence of an equilibrium of active and inactive molecules of the ester substrat, such as had earlier been suggested by Arrhenius to account for the high temperature coefficient of such reactions, was rendered improbable and that an explanation of neutral salt action would probably be such as involves only the catalyzing liquid and not the ester present.

It was next shown³ that the experimental results of simple acid catalysis and of the accelerating influence of neutral salts in aqueous solutions could be interpreted more closely than was hitherto possible, and with an accuracy as considerable as the present fairly large experimental error will permit, if the activity of the undissociated molecule be assumed. Also, the relation of Snethlage between activity and strength of acid was shown to be applicable in aqueous solutions.

These conclusions received independent confirmation in a research of Dawson and Powis⁴ on the catalytic influence of acids on the keto-enol transformation of acetone in aqueous solutions. With the aid of the then available literature the author was led⁵ to the formulation of a quantitative relation between catalytic ratio of undissociated molecule and hydrogen ion activities and the affinity constants of various acids. It was suggested that a simple mathematical relationship, *viz.*, that the affinity constant was equal to the square of the catalytic ratio, existed between the two; that the strength of the acid is the primary factor in the determination of the catalytic ratio and that deviations from the values calculated according to the equations deduced in the paper should be sought for in the variations of the nature of the reaction studied.

Somewhat later,⁶ MacBain and Coleman, in a recalculation of some old data of Arrhenius on the dissociation of weak acids, called attention to the

¹ *Am. Chem. J.*, **48**, 352 (1912).

² *Medd. fr. K. Vetenskaps. Nobelinst. Bd. 2*, Nr. 34 (1913).

³ *Loc. cit.*, Nr. 37 (1913).

⁴ *J. Chem. Soc.*, **104**, 2135 (1913).

⁵ *Z. Elektrochem.*, **20**, 201 (1914).

⁶ *J. Chem. Soc.*, **105**, 1520 (1914).

fact that some measurements of Arrhenius on the inversion of cane sugar by hydrochloric acid, in presence and absence of potassium chloride at varying temperatures, could be used for the determination of the ratio $K_m : K_h$.¹ These data, while revealing internal evidence of a certain amount of experimental error, made it appear probable, according to the authors, that the ratio K_m/K_h decreases with rise of temperature. The actual figures are given in Table I.

TABLE I.

| Potassium chloride. | 0.05N HCl at 25°. | 0.01N HCl at 38°. | 0.0005N HCl at 52°. |
|------------------------|----------------------|----------------------|------------------------|
| 0.025 | 2.99 | 1.45 | 1.13 |
| 0.125 | 2.77 | 1.70 | 1.30 |

It was further suggested that this effect had not hitherto been suspected and might serve to explain some of the deviations from the quantitative relationship proposed somewhat earlier by the author. Actually, however, the point in question had been noted and the same calculations had been made with essentially the same result, but it was felt that, in view of the extraordinary sensitivity of the ratio to small experimental errors as evidenced by the author's own results under more favorable conditions, it would be better to defer discussion of the point until some more definite evidence was accumulated. Certain experiments were, however, carried out in the laboratory of Arrhenius by the author having a bearing on the point in question, which will be presented below, together with other experimental data just available from the literature. MacBain and Coleman nevertheless point out later in their paper that, if a constant value for K_m/K_h of 1.5 is applied throughout their calculations for all temperatures, all the results with the exception of the first three are within 4% of the predicted rates; and that of the three discordant experiments one diverges as much in one direction as another does in the opposite. It is obvious, therefore, that a decision as to whether the catalytic ratio is a variable with temperature remained, as a result of MacBain and Coleman's investigations, an open question.

There has recently appeared² a paper on catalysis which supplies data utilizable for a calculation of the temperature influence in ester catalysis as regards the catalytic ratio. The hydrolysis of methyl acetate at vary-

¹ The reaction constant is regarded as due to the sum of two catalytic activities, that of the hydrogen ion K_h and that of the undissociated acid K_m . These activities are regarded as operating in degrees proportional to their concentrations as calculated from the conductivity data. An equation is obtained of the form

$$n_h K_h + n_m K_m = R$$

where n_h or n_m are the respective concentrations of ion or molecule, R the reaction constant. From two such equations K_m and K_h may be evaluated and the catalytic ratio, $K_m : K_h$ obtained.

² Lamble and Lewis, *J. Chem. Soc.*, 105, 2330 (1914).

ing concentrations of hydrochloric acid has been studied at 25° and 35° and the degrees of dissociation and hydrogen ion concentrations of the acids employed have been obtained. The range of concentrations chosen was large and the data obtained seemed to offer a good opportunity for making the calculations required. The general conclusion is drawn that there is no tendency at all for the temperature-coefficient of a strongly catalyzed reaction to be less than that of a weakly catalyzed reaction, a deduction contrary to what one would have expected on the conception of active and inactive molecules of ester substrat, in agreement, therefore, with the earlier conclusions of the author from work on neutral salt action with varying ester.

The experimental results of Lamble and Lewis have been calculated to give the values of K_m and K_h and the ratio K_m/K_h at the two temperatures employed. The method of calculation has been described in detail in various earlier communications so that it calls for no further detailment here. The six possible combinations of pairs of data as to molecular and ionic concentrations and to catalytic activity at each temperature have been calculated and the results are set forth in Table II.

TABLE II.

| | 25°. | | | 35°. | | | From expts. | 25° K_m/K_h | 35° K_m/K_h |
|---|----------------------|-----------------------------|--------------------|----------------------|-----------------------------|--------------------|----------------|---------------|---------------|
| | Acid nor- mality. | H ⁺ ion conc. | Reaction const. | Acid nor- mality. | H ⁺ ion conc. | Reaction const. | | | |
| | 0.5024 | 0.4503 | 3.510 | 0.5024 | 0.4400 | 8.836 | 1 & 2 | 1.94 | 4.62 |
| 2 | 0.8275 | 0.7047 | 6.001 | 0.8275 | 0.7086 | 15.26 | 1 & 3 | 4.60 | 1.88 |
| 3 | 1.800 | 1.422 | 16.09 | 1.935 | 1.422 | 37.84 | 1 & 4 | 2.36 | 1.91 |
| 4 | 2.429 | 1.718 | 20.78 | 2.92 | 1.718 | 63.47 | 2 & 3 | 9.62 | 1.54 |
| | | | | | | | 2 & 4 | 0.945 | .77 |
| | | | | | | | 3 & 4 | —0.71 | .95 |

If the theory of Goldschmidt, Snethlage and Acree be correct, it is obvious that the ratio K_m/K_h as calculated from a series of acid dilutions should be constant. Observation will show that at 35° with one exception, in which experimental errors would certainly be greatest in their effect on the calculation, the requirement is fulfilled. At 25° it will readily be seen that the values obtained are by no means constant. Closer examination reveals, however, that only those calculations in which Expt. 3 was utilized were the deviations considerable, yielding in the one case a negative result. The experimental results were therefore examined more closely and led to the conclusion that in all probability some fairly considerable error had crept into the determination. For example, it is well known—and the data of Lamble and Lewis confirm this—that the reaction constant in catalysis of esters by hydrochloric acid increases at a slightly more rapid rate than does the normality of the acid; in other words, the

graph of the two sets of values yields a curve concave towards the axis of normality. Lamble and Lewis' results were plotted therefore in this manner and the plot for Expt. 3 was found to lie some considerable distance from the curve through the remaining points and concave to the axis of normality. Fortunately a determination made by the authors at a concentration 0.1024 *N* could be included to facilitate this conclusion. Further, an examination of the values used for the degree of dissociation at the concentration employed in Expt. 3, *viz.*, 1.80 *N*, showed the rather surprising result that the degree of dissociation at 1.80 *N* was equal to that at 1.28 *N* and amounted to 0.7900, while at a concentration 0.6 *N* higher the dissociation had fallen rapidly again to 0.7071. It is not surprising, therefore, that with two such factors operating in the calculations the results obtained should show some irregularity. Of the remaining three it cannot be said, however, that they show values higher than those obtained in the calculations at 35°. The mean of the three calculations at 25° is 1.75 while of the five concordant values at 35° the mean is 1.81.

Happily, however, a surer test than the above may be applied to the question of the variability or non-variability of the ratio K_m/K_h with temperature. Dawson and Powis obtained in their investigations a most excellent series of values for K_m and K_h at 25° with hydrochloric acid, yielding as a mean value from a series of seven observations 1.77 for the catalytic ratio. This value is in remarkably good agreement with the value calculated from the data of Lamble and Lewis at the two temperatures.

It would seem, therefore, that the suggestion of MacBain and Coleman as to the decrease of the activity ratio with temperature is untenable in the light of the above results. Confirmation of this view seems forthcoming in the data presented below, compiled from experimental work of the author. In some earlier work on neutral salt action in ester catalysis it had been noted that, according to Price¹ and Senter² the action is not markedly influenced by temperature. That conclusion was tested experimentally by the author over a wider range of temperature than had previously been employed. The velocity of hydrolysis of ethyl acetate using 0.1 *N* hydrochloric acid, alone and in presence of normal potassium chloride, was studied at the three temperatures 0°, 25°, and 40°. The experimental values communicated below represent the means of at least two concordant experiments. The value *D* expresses the percentage increase in the reaction constant due to the presence of the salt, assuming that the change in the reaction constant is proportional to the change of hydrogen ion concentration.³

¹ *Ofvers. af Vet. Akad. Forh.*, 9, 934 (1899).

² *Z. physik. Chem.*, 70, 516 (1910).

³ Kay, *Proc. Roy. Soc. Edin.*, 22, 484 (1897); Taylor, *loc. cit.*, No. 34.

TABLE VI.

| Temp. | Normality of acid. | Normality of neutral salt. | Velocity constant. K_v | Hydrogen ion concentration, α . | $D = 100 \frac{K_1 - K_1 \alpha_1 / \alpha_2}{K_1 \alpha_1 / \alpha_2}$ |
|-------|--------------------|----------------------------|-----------------------------|---|---|
| 0° | 0.10 | ... | 2.056 | 0.916 | |
| | 0.10 | 1.0 | 2.480 | 0.777 | 42.2 |
| 25 | 0.10 | ... | 28.29 | 0.916 | |
| | 0.10 | 1.0 | 34.45 | 0.777 | 43.6 |
| 40 | 0.10 | ... | 109.4 | 0.916 | |
| | 0.10 | 1.0 | 132.9 | 0.777 | 43.2 |

Assuming, therefore, as has frequently been shown, that at these concentrations the degree of dissociation of the acid varies but slightly with temperature, it is obvious that the values for K_m/K_h obtained at the various temperatures will also be concordant. In other words, as pointed out previously by the author, the ratio of the catalytic activities of undissociated molecule and hydrogen ion is primarily a function of the strength of the acid and therefore of its dissociation constant when such can be derived; that therefore, since the dissociation constant varies but little with temperature, the catalytic ratio will itself be relatively independent of temperature and not, as originally suggested by MacBain and Coleman, possess a large temperature coefficient.

Attention might here be directed also to the method employed by Lamble and Lewis for the determination of the temperature coefficient of these reactions. As pointed out by them, so long as the same hydrogen ion concentration persists at the two temperatures in the corresponding experiment, the concentration of the catalyst remains the same, whether the catalyst be the hydrogen ions, the undissociated molecules or both. But at the higher concentrations employed by them the condition is no longer fulfilled, for a hydrogen ion concentration of 1.422 corresponds to a 1.800 *N* acid at 25° and to a 1.935 *N* acid at 35°. It is evident, therefore, that if the undissociated molecule be considered active, then of the two solutions, at the same hydrogen ion concentration, the acid of normality 1.935 at 35° will be the more active, since its concentration will be 0.513 in respect to undissociated molecule, as compared with 0.378 in the case of the acid of normality 1.800 at 25°. Since the undissociated molecule appears from the previous calculations to be 1.8 times as active as the hydrogen ion, it is evident that the temperature coefficient K_{35}/K_{25} , as deduced by them, is in reality a little too large as the total concentration of catalyst is greater at the higher temperature. If this factor is taken into consideration, and the reaction constant at 25° be re-checked, it is very probable that the temperature coefficient K_{35}/K_{25} at the two higher concentrations would more closely correspond with the very concordant value found by them in the more dilute solutions, where no divergence exists between acid normality and hydrogen ion concentration at the two temperatures.

Summary.

An examination of recently available literature on catalysis of esters at varying temperatures, together with some new experimental data on neutral salt action in ester catalysis at 0°, 25°, and 40° is shown to yield the conclusion that the ratio of the catalytic activities of undissociated molecule and hydrogen ion does not possess a considerable temperature coefficient such as was suggested by MacBain and Coleman, but, on the contrary, is independent of temperature. The importance of a consideration of the activity of the undissociated molecule in calculations of reaction constants in acid catalyses has been emphasized.

PRINCETON, N. J.

ORGANIC OXONIUM COMPOUNDS.

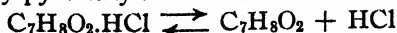
I. DIMETHYLPYRONEHYDROCHLORIDE.

By H. N. K. RÖRDAM.

Received January 6, 1915.

Theoretical Part.

Since the discovery by Collie and Tickle¹ of the addition compounds of dimethylpyrone with acids, numerous investigations have been made upon this matter. That these and similar addition products of organic compounds containing oxygen are real and stable compounds and chemical individuals has been shown in researches by several authors, among many others recently by Kendall,² and Maas and McIntosh.³ As to their being oxonium compounds, the question is still open. Not one single experimental fact is known, which absolutely compels us to see in them anything more than molecular compounds in which the acid is bound in the manner that the water of crystallization is in crystallized salts. If the addition compounds with acids are true oxonium compounds, they must be salts; but although many observations have been made which may suggest a salt character, only evidence, not certainty, has been won. The conductivities of these compounds as well as the depression of the freezing point of their solutions have been measured by several investigators. It was found that their solutions were conductive, and that the freezing point was more depressed than the number of dissolved mols would account for. From these measurements constants of dissociation for dimethylpyrone as a base were calculated. It is, however, evident that the results would be the same if only dissociation into components, for instance for dimethylpyronehydrochloride after the scheme:



takes place in the solutions. To prove that dimethylpyronehydrochloride is a real salt it must first be proved that, besides the above-named

¹ *J. Chem. Soc. Trans.*, 1899, 710.

² *THIS JOURNAL*, 36, 1222.

³ *Ibid.*, 34, 1273 and 35, 535.

hydrolytic dissociation into components, also electrolytic dissociation of the hydrolytically undissociated part takes place in solutions according to the scheme:



This has not yet been proved.

Nevertheless in modern textbooks the quadrivalence of oxygen is often treated as a matter of fact equal to the pentavalence of nitrogen, but this is due to a wrong estimation of some experimental results, the essentials of which I shall hereby briefly summarize, the question being about as important a matter as the supplementing of the theory of valency.

Coehn¹ has by means of migration measurements tried to demonstrate the presence of the ion



in solutions of dimethylpyrone into hydrochloric acid (20% HCl). He found that dimethylpyrone was carried to the cathode, but in one of the two experiments which he made, the electrode spaces were separated from the rest of the solution by parchment membranes, so that it was not excluded that electric endosmose might have taken place. Therefore Coehn made another experiment without membranes. When the electrolysis was finished, the contents of the electrode spaces were removed, and phosphotungstic acid was added, whereby dimethylpyrone is precipitated. The precipitate was not isolated or determined in any way, as was the case in the first of the two experiments; the author only reports that it could be directly seen that there was more of it in the cathode room than in the anode space. The omission of weighing the precipitate deprives this investigation of its significance, and moreover, among others, Coehn² himself has shown that non-electrolytes also can migrate under the influence of the electric current. For instance, cane sugar in hydrochloric acid will migrate to the cathode without the conductivity of the acid being altered more than the trifle which is due to the alteration of viscosity of the solution.

Walden's³ investigations mainly include:

1. The depression of the freezing point in solutions of dimethylpyrone and of dimethylpyrone + hydrochloric acid in water.
2. The conductivity of picric acid in water and of picric acid + dimethylpyrone in water.

These two series of experiments showed that part of the acid (picric or hydrochloric) was linked to the dimethylpyrone, and from the results Walden calculates the constants of hydrolytic dissociation for the oxonium salt which I have put together in the following table under K^{I} and K^{II} .

¹ *Ber.*, 35, 2673.

² *Z. f. Elektrochemie*, 1909, 652.

³ *Ber.*, 34, 4185.

| K ^I . | K ^{II} . | K ^{III} . |
|-------------------|-------------------|--------------------|
| 0.648 | 0.59 | 0.72 |
| 0.373 | 0.45 | 0.60 |
| 0.340 | 0.53 | 0.62 |
| ... | 0.50 | 0.52 |
| Average..... 0.45 | 0.52 | 0.61 |

These constants have been calculated under assumption of electrolytic dissociation. Thereafter also an electrolytic dissociation constant for dimethylpyrone as a base is calculated by means of the equation:

$$K_{\text{hydrolytic}} = \frac{\text{constant of electrolytic dissociation for water}}{\text{constant of electrolytic dissociation for the base}}$$

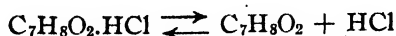
From the concordance between the values of the two series of hydrolytic constants (and consequently also electrolytic constants) found by different ways, one cannot, however, in this case deduce the correctness of the hypothesis (electrolytical dissociation), since a hydrolytic constant calculated under the assumption of dissociation into components only is of about the same amount, and the single values show as much conformity as do K^I and K^{II}. I have calculated this series of constants from the experiments under 2 (conductivity) and put them down in the table under K^{III}.

3. The conductivity of dimethylpyrone in liquid SO₂ was examined. The molecular conductivity was found to increase with increasing dilution, a fact that suggests the formation of a salt.

4. The conductivity of dimethylpyrone and tribromoacetic acid separately and mixed together. Separately both showed a very small conductivity, together a considerably greater. But the molecular conductivity *decreased* with increasing dilution.

Obviously there are things in these investigations which may suggest the formation of a salt in the above-mentioned cases, but none of them offers a stringent proof.

It must, however, be possible to decide absolutely the question by measuring the concentrations of H ions and of Cl ions in an aqueous solution of dimethylpyronehydrochloride. If only dissociation into components:



takes place then the H ion concentration must be equal to the Cl ion concentration, as both kinds of ions then will originate only from the acid set free by the hydrolysis. The dimethylpyronehydrochloride will in this case be a molecular compound.

If the product is a salt, then the Cl ion concentration must be greater than the H ion concentration, for besides the Cl ions which originate from the free acid:



there must also be Cl ions originating from the salt:



The Cl ion concentration can be determined with sufficient accuracy by measuring the potential difference between the solution and a Hg/HgCl electrode. The determination of the H ion concentration by measuring the potential difference between the solution and a H electrode had to be given up, for it turned out by experiments I made that the dimethylpyrone was decomposed by the hydrogen. But the H ion concentration can be determined in other ways. The question is only to choose a method which affords the necessary accuracy. The colorimetric method will according to Sorensen¹ only allow an accuracy of ± 0.1 in the H ion exponent ($= -\log(\text{H}^+)$). In a 0.1 *N* solution the degree of hydrolytic dissociation of dimethylpyronehydrochloride is about 0.85 according to the experiments of Walden.

If the electrolytic dissociation of hydrochloric acid is estimated to be complete into a 0.1 *N* solution, then the question will be of the determination of the difference between two H ion exponents which in the highest can be:

$$\log 0.1 - \log 0.085 = 0.07.$$

In other words, the quantity that should be determined is of about the same amount as the uncertainty of the measurement. The colorimetric method is then unfit for use in this case. A more accurate method we have in measuring the catalysis of the saponification of diazoacetic ester, but this method is unsuitable in this case, as Bredig and Ripley² have shown that it cannot be employed when only a trace of Cl ion is present.

While the determination of the conductivity alone cannot solve the problem, as I have shown above, determinations of the conductivity combined with determinations of the Cl ion concentration will answer the purpose.

A solution of dimethylpyronehydrochloride and a solution of hydrochloric acid, whose Cl ion concentrations electrometrically measured are equal, will have the same conductivity, if the dimethylpyronehydrochloride is only dissociated into components. If, on the contrary, also electrolytic dissociation takes place, then the molar conductivity of the dimethylpyronehydrochloride solution will be smaller than the mol. conductivity of the hydrochloric acid solution, for the Cl ion concentrations are equal in both solutions, but in the pyrone solution a part of the fast-migrating H ions are replaced by the much slower migrating dimethylpyrone ions.

¹ "Ueber die Messung und Bedeutung der Wasserstoffjonenkonzentration bei biologischen Processen," S. 428.

² *Ber.*, 40, 4015.

This is seen most distinctly when the experimental results are plotted in a diagram. Plotting corresponding values of molecular conductivity against electrometrically measured Cl ion concentration the result will be one single curve common for the pyrone solution and the hydrochloric acid, if dissociation into components only takes place. In case of electrolytic dissociation of the non-hydrolyzed part two separate curves will result, the curve for hydrochloric acid lying higher than the other. They will unite at the point which gives the molecular conductivity of hydrochloric acid at ∞ dilution (Cl ion concentration = 0) and will separate more and more with increasing concentration.

Experimental.

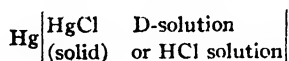
Consequently my experiments included electrometric determination of Cl ion concentration and of conductivity. The solutions of dimethylpyronehydrochloride, which in the following I shall simply call D-solutions, were made by dissolving accurately weighed quantities of crystallized $C_7H_8O_2.HCl.2H_2O$.

The strength of the hydrochloric acid, of which I measured the conductivity and Cl ion concentration, was determined by adding a small excess of silver nitrate to 20 cm³. of the acid and reducing the precipitated AgCl in hydrogen. The result was

$$1.1932 \text{ g. Ag}$$

wherefrom the strength of the acid is found to be 0.4424 *N*. The other solutions were produced by dilution by means of an accurate pipet (Geissler).

To the determination of the Cl ion concentration four half-elements of the type:



were constructed for each dilution.

They were measured by the compensation method (Poggendorff) against a 0.1 *N* Hg, HgCl electrode, a 3.5 *N* KCl solution and a 1.75 *N* KCl solution being successively used to produce the contact between the two electrode solutions in order to eliminate the diffusion potential. During the measuring the elements were placed in a water-thermostat, the temperature of which did not alter more than 0.1°. Until the measurements were made, the syphon tubes of the electrodes dipped into small glasses holding the same solution as in the electrode spaces in order to prevent the concentration from altering by evaporation.

The results of the measurements are collected in the following Tables I and II. Under [Cl⁻] the Cl ion concentration calculated from the potential difference. By means of Nernst's equation:

$$\pi = \frac{RT}{0.4343e} \cdot \log \frac{c_1}{c_2},$$

which holds for the potential difference after the diffusion-potential has been eliminated, and where c_1 and c_2 mean the concentrations of Cl ions, respectively, in the D-solution (or the HCl solution) and in the 0.1 *N* KCl solution is found at 19.8°.

$$\log [\text{Cl}^-] = \frac{\pi}{0.0581} + \log 0.085.$$

TABLE I.

(D-solutions; $t = 19.8^\circ$.) π (average of 4 elements).

| Concentration of the solution. | Contact produced by | | Extrapolated. | [Cl ⁻]. |
|--------------------------------|---------------------|--------------------|---------------|---------------------|
| | 3.5 <i>N</i> KCl. | 1.75 <i>N</i> KCl. | | |
| 0.3750 <i>N</i> | 0.0372 Volt | 0.0428 Volt | 0.0316 Volt | 0.2974 |
| 0.2813 <i>N</i> | 0.0289 | 0.0342 | 0.0236 | 0.2227 \times |
| 0.1969 <i>N</i> | 0.0218 | 0.0263 | 0.0175 | 0.1667 \times |
| 0.09646 <i>N</i> | 0.0045 | 0.0079 | 0.0011 | 0.0888 |
| 0.06608 <i>N</i> | -0.0048 | -0.0019 | -0.0077 | 0.0627 |
| 0.02500 <i>N</i> | -0.0291 | -0.0270 | -0.0312 | 0.0247 |

TABLE II.

(HCl solutions; $t = 19.8^\circ$.) π (average of 4 elements).

| Concentration of HCl solution. | Contact produced by | | Extrapolated. | [Cl ⁻]. |
|--------------------------------|---------------------|--------------------|---------------|---------------------|
| | 3.5 <i>N</i> KCl. | 1.75 <i>N</i> KCl. | | |
| 0.4424 <i>N</i> | 0.0415 Volt | 0.0493 Volt | 0.0336 Volt | 0.3219 |
| 0.3318 <i>N</i> | 0.0339 | 0.0412 | 0.0265 | 0.2432 |
| 0.2212 <i>N</i> | 0.0236 | 0.0295 | 0.0177 | 0.1694 \times |
| 0.1769 <i>N</i> | 0.0172 | 0.0228 | 0.0115 | 0.1395 \times |
| 0.1327 <i>N</i> | 0.0110 | 0.0158 | 0.0062 | 0.1117 \times |
| 0.1106 <i>N</i> | 0.0074 | 0.0116 | 0.0032 | 0.0963 |
| 0.04430 <i>N</i> | -0.0143 | -0.0121 | -0.0165 | 0.0442 |
| 0.02210 <i>N</i> | -0.0307 | -0.0287 | -0.0326 | 0.0233 |

The extrapolated potential and the Cl ion concentration is shown in Figs. 1 and 2 by the curves π and [Cl⁻]. Between the points the curve has been drawn by help of a flexible ruler whereby the \times -marked values of [Cl⁻] have been graphically corrected.

The conductivity of the D-solution was measured at 18.0° and at 19.0°; in Table III the values of Λ 19.8° marked with \times are directly measured, the others calculated by help of the temperature coefficient from the values under Λ 18.0°, which are all directly measured. For the hydrochloric acid the conductivity has been determined only at 19.8°. Between the points so determined the curve has been drawn in as good accordance as possible with the 18.0° curve, the values of which are taken from Kohlrausch and Holborn: "Leitfähigkeit der Elektrolyte."

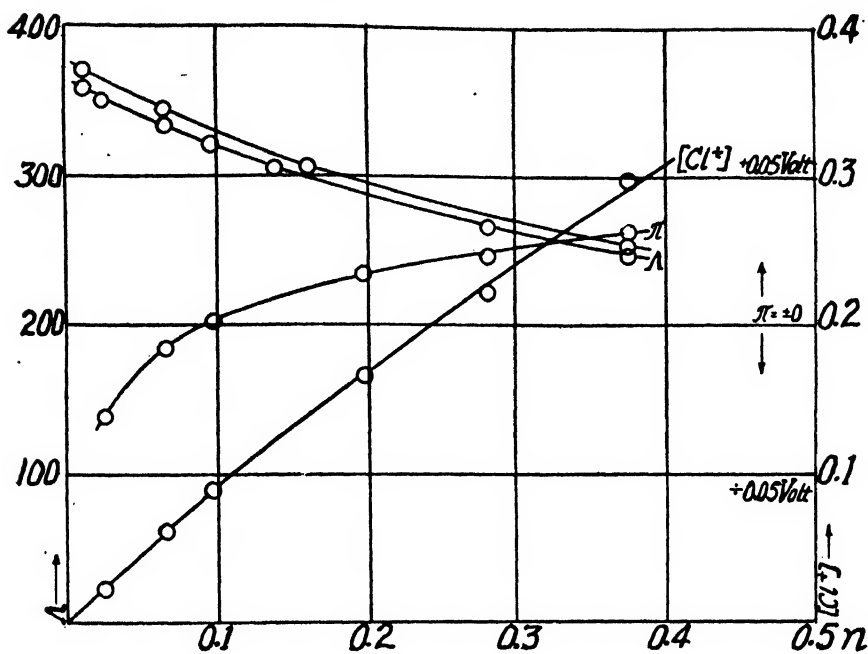


Fig. 1.—D-solution.

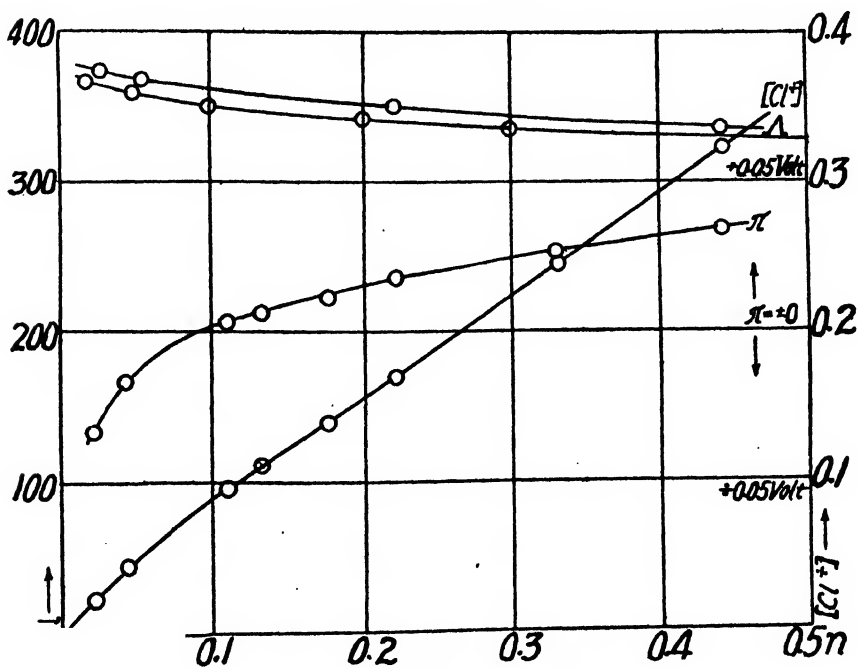


Fig. 2.—Hydrochloric acid.

In Table IV the directly measured values are marked with x .

TABLE III.
D-solutions.

| Conc. | $\Lambda_{18.0^\circ}$ | $\Lambda_{19.8^\circ}$ |
|--------|------------------------|------------------------|
| 0.3750 | 247.2 | 253.4 x |
| 0.2813 | 267.1 | 273.1 |
| 0.1969 | 289.8 | 294.5 |
| 0.1574 | ... | 306.5 x |
| 0.1378 | 305.9 | 314.8 |
| 0.0965 | 321.4 | 331.9 |
| 0.0661 | 334.5 | 345.0 x |
| 0.0250 | 350.7 | 364.2 |
| 0.0125 | 358.5 | 370.5 x |

TABLE IV.
HCl solutions.

| Conc. | $\Lambda_{19.8^\circ}$ |
|--------|------------------------|
| 0.4424 | 335.4 x |
| 0.3318 | 341.8 |
| 0.2212 | 350.9 x |
| 0.1769 | 354.0 |
| 0.1327 | 358.3 |
| 0.1106 | 361.0 x |
| 0.0553 | 368.4 x |
| 0.0443 | 370.7 |
| 0.0277 | 374.1 x |
| 0.0221 | 375.7 |

In Figs. 1 and 2 the conductivities are shown by the curves Λ ; the upper one holds for 19.8° , the lower one for 18.0° .

Finally corresponding values of Cl ion concentration and mol. conductivity are plotted together into Fig. 3, respectively, for D-solutions (curve Λ_D) and for hydrochloric acid (curve Λ_{HCl}). As deduced in the theoretical part the shape of these two resulting curves affords a stringent

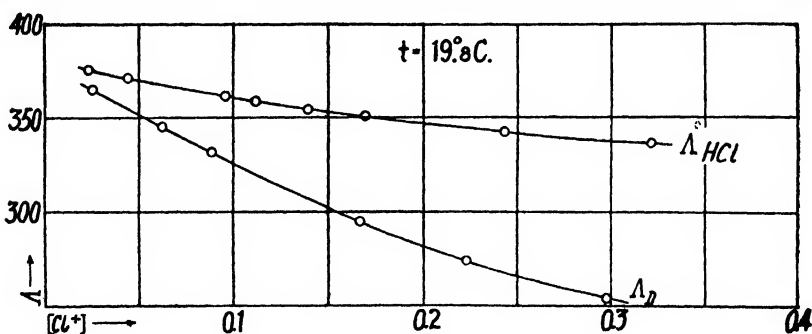


Fig. 3.

proof that in aqueous solutions of dimethylpyronehydrochloride electrolytical dissociation of the non-hydrolyzed part of the addition compounds takes place, so that *dimethylpyronehydrochloride* is a real salt and consequently an atomistic compound.

Discussion of the Results.

The equation by means of which the Cl ion concentration has been calculated from the potential only holds for diluted solutions, as it is based upon the applicability of the gas laws upon the dissolved substance. Consequently only that part of the curves which corresponds to concentrations smaller than 0.1 N gives the exact values of the Cl ion concentration.

For the higher concentrations the method of calculation employed will not give the absolutely correct values of the Cl ion concentration. Still the values can very well be used for comparison, since we must take it for granted that the same Cl ion concentration will give the same potential difference against a Hg/HgCl electrode, even if the relation between these two quantities is not expressed by the Nernst equation.

The experimental error in the determination of the molecular conductivity is about $\pm 0.5\%$. The alterations which might arise in the viscosity or possibly in the dielectric constant of the solvent by the presence of dimethylpyrone have been estimated to be of no importance in this case. The experimental error in the determination of the potential difference arises mainly from the elimination of the diffusion potential. Even in concentrations below $0.1 N$ it ought to be estimated as at least ± 0.5 millivolt, which gives an error in $[Cl^-]$ of about $\pm 2\%$, but it can increase to double the amount, if special precautions are not taken. From the diagram it is evident that errors of this amount will not alter the shape or the reciprocal situation of the curves.

The determination of the potential difference is in itself uncertain for concentrations over $0.1 N$, for the elimination of the diffusion potential will here involve an increasing error, but at the same time the differences between the corresponding conductivities increase so strongly, as may be seen in Fig. 3, that the reciprocal situation of the curves doubtless is correct also for this part.

As the salt character of the addition compound has hereby been proved, the calculation of a base constant for dimethylpyrone is now legitimate. Walden¹ from his conductivity measurements of the picrate calculated:

$$K_b = 2.4 \times 10^{-14}$$

by means of Bredig's table over the range between the molecular conductivity of a salt at ∞ -dilution and the molecular conductivity at lesser degrees of dilution. He ascribed to the dimethylpyrone ion the velocity of migration: 35 = the velocity of migration of organic bases of similar constitution (tertiary, cyclic, containing 18 atoms).

Without help of Bredig's table² the dissociation constant can be calculated in the following way, when the Cl ion concentration is known both for D-solution and for HCl solutions.

By comparing the molecular conductivities of a D-solution and a HCl solution, both with the same Cl ion concentration, it is evident that the ratio of the difference δ between these two conductivities and the difference which would arise, if all H ion was linked under formation of dimethylpyrone ion is

¹ *Loc. cit.*

² *Z. physik. Chem.*, **13**, 191 (1894).

$$= \frac{\delta}{\gamma(\Lambda_H - \Lambda_D)} = \text{the degree of association}$$

= 1 — the degree of hydrolysis. Then the degree of hydrolysis is:

$$\alpha = 1 - \frac{\delta}{\gamma(\Lambda_H - \Lambda_D)} = \frac{\gamma(\Lambda_H - \Lambda_D) - \delta}{\gamma(\Lambda_H - \Lambda_D)}$$

wherein Λ_H means the velocity of migration of H ion, Λ_D the velocity of migration of dimethylpyrone ion which, like Walden, I estimate to 35— γ is the degree of dissociation of the hydrochloric acid and it is supposed that a non-hydrolyzed dimethylpyronehydrochloride solution would have the same degree of dissociation, a supposition which can involve no remarkable error.

By this the following values are calculated:

| Strength of the solution. | α . | Constant of hydrolysis. |
|---------------------------|------------|-------------------------|
| 0.100 | 0.88 | 0.63 |
| 0.0661 | 0.92 | 0.68 |
| 0.0250 | 0.96 | 0.59 |

Average, 0.63

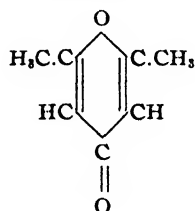
from which the constant of dissociation for dimethylpyrone as a base is found:

$$K_b = 1.9 \times 10^{-14}$$

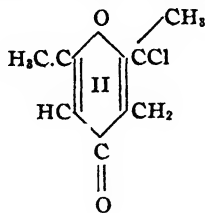
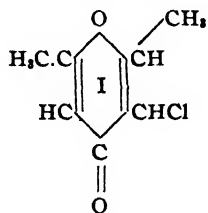
of about the same amount as the constant calculated by Walden.

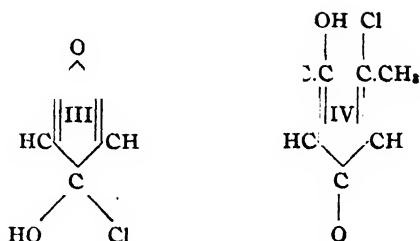
After this there can be no serious doubt about the configuration formula of the dimethylpyronehydrochloride.

The configuration of dimethylpyrone itself is:

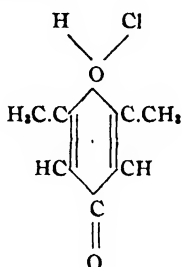


The possibilities for the formation of an addition compound with one molecule HCl, excluding the oxonium formula, are:





All of them have been discussed and some of them defended, but surely not one of them can account for electrolytic dissociation, so that the oxonium formula must be correct:



I am going to extend these investigations to the addition compounds of ethers with acids. The simple structure of the ethers will entail that the structure of the addition compounds is quite doubtless, if they turn out to be salts like dimethylpyronehydrochloride.

POLYTECHNICAL HIGH SCHOOL,
COPENHAGEN, DENMARK.

THE PRODUCTION OF CHLOROPICRIN BY THE ACTION OF AQUA REGIA ON ORGANIC COMPOUNDS.

[PRELIMINARY PAPER.]

BY RASIK LAL DATTA AND NIHAR RANJAN CHATTERJEE.

Received January 12, 1915.

Aqua regia has been found to be a chlorinating¹ as well as an oxidizing agent.² It has now been found that it sometimes acts destructively, leading to the rupture of organic substances subjected to its action, with the production of chloropicrin. The transformation into chloropicrin is quantitative in some cases, in others it takes place to a limited extent while in some cases it does not take place at all. The action of aqua regia on the following substances has been studied.

Acetone.—Aqua regia decomposes acetone almost quantitatively into chloropicrin and the reaction can therefore be employed as the best method

¹ Datta and Fernandes, *THIS JOURNAL*, 36, 1007 (1914).

² Datta, *Ibid.*, 36, 1011 (1914).

for the laboratory preparation of this substance. Hofmann¹ gave a laboratory method for the preparation of this compound by the action of bleaching powder on picric acid. This procedure, however, gives only poor yields and is troublesome to carry out.

To a mixture of 2 parts of nitric acid and 3 parts of hydrochloric acid, acetone is gradually added, the acid mixture being warmed slightly. An oil separates at first, which soon dissolves with the production of the characteristic odor of chloropicrin. The addition of acetone is stopped when a quantity equal to a tenth part of the acid mixture has been added. When the whole of the acetone has been added the mixture is warmed on the water bath for some time to enable the reaction to become complete. The resulting liquid is next subjected to steam distillation and the compound is separated, dried by means of calcium chloride and finally distilled at a slightly reduced pressure.

The substance boiled between 113–114° at about 750 mm. The yield obtained was 85% of the theory. To establish its identity a chlorine determination was made.

0.1661 gave 0.4288 AgCl. Calc. for CCl_3NO_2 : Cl, 64.74; found: 63.86.

It has been observed that if the reaction is carried out in the cold, with very gradual addition of acetone, an oil containing chloropicrin separates, which, on slow evaporation in a desiccator, yields colorless crystals having m. p. 103–104°. This is being investigated.

Allyl Alcohol.—The action of aqua regia on allyl alcohol was next studied, in as much as it contains an unsaturated bond. When the reaction was carried out with warming, quantitative production of chloropicrin was the result; but when it was carried out in the cold, a mixture of chloropicrin and another substance which is under investigation was produced. Allyl alcohol was gradually added to a mixture of the acids (2:3), with occasional warming on the water bath. Its transformation into chloropicrin was complete. The resulting solution was subjected to steam distillation. A colorless oil was obtained which was identified by distillation as usual.

Ether.—When ether was added in small portions to aqua regia no change was apparent at first, but on warming limited action took place. At the end of the reaction no oil was deposited, a pungent odor of chloropicrin being noticed as usual. The product was separated by steam distillation and it was found that a very small quantity of chloropicrin had been formed.

Ethyl Alcohol.—Ethyl alcohol is decomposed only partially with the formation of chloropicrin. To a mixture of nitric and hydrochloric acids (2.3), ethyl alcohol was added in small quantities. At first no reaction took place, but after a time the action became violent and the

¹ *Ann.*, 139, 111 (1866).

acid mixture had to be cooled. After the action had subsided the mixture was warmed on the water bath for a few minutes. The chloropicrin was recovered as usual after steam distillation.

Methyl Alcohol.—Methyl alcohol remains undecomposed by aqua regia even on warming on the water bath and hence no chloropicrin is produced. After a very prolonged action only a slight smell of chloropicrin could be noticed.

Formic and Acetic Acids.—These acids are quite stable and remain undecomposed even on warming. Consequently no chloropicrin is formed in these cases.

A host of other substances has been found to give chloropicrin as the ultimate decomposition product, and it appears that the production of chloropicrin might be quite general. Investigations to establish this as well as a general study of the action of aqua regia and also the action of nitric acid in conjunction with bromine and iodine on organic bodies are being continued.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

CONTRIBUTIONS TO THE KNOWLEDGE OF HALOGENATION. VII.¹ SUBSTITUTED NITROGEN CHLORIDES. THE ACTION OF CHLORINE ON CARBAMIC ESTERS AND BIURETS AND THE PREPARATION OF CHLOROCAR- BAMIC ESTERS AND CHLOROBIURETS.

BY RASIK LAL DATTA AND SATYARANJAN DAS GUPTA.

Received January 12, 1915.

The action of chlorine on ethyl carbamic ester has been studied by us² with the isolation of monochlorocarbamic ester. Schmidt³ obtained a condensation product of urethane with dichloroacetaldehyde, *viz.*, dichloro-ethylidene urethane by the action of the same reagent on the ester at a high temperature.

It has been found that the chloroderivatives of other esters of the series can be prepared by working with aqueous solutions of the urethanes in the cold. These have been specially isolated since they might serve as useful synthetic reagents on account of their greater stability than similarly substituted carbamide derivatives. It has been noted under monochlorocarbamic ester, that it readily serves for the chlorination of amines and amides which hitherto had to be chlorinated by means of alkaline

¹ Previous communications on the subject; see Datta, *J. Chem. Soc.*, 101, 166 (1912); Datta and Ghosh, *THIS JOURNAL*, 35, 1044 (1913); Datta and Gupta, *Ibid.*, 36, 386 (1914); Datta and Fernandes, *Ibid.*, 36, 1007 (1914); *Ibid.*, 36, 1011 (1914); Datta, *Ibid.*, 36, 1011 (1914).

² Datta and Gupta, *THIS JOURNAL*, 36, 386 (1914).

³ Schmidt, *J. prakt. Chem.*, [2] 24, 120 (1881).

hypochlorites. Besides, it has also been found that the monochloro-carbamic esters hydrolyze, giving rise to interesting condensation products. These compounds have been found to be extremely active, the chlorine in them being very loosely combined and they react vigorously with sodium. In fact these compounds promise to be of signal service in as mild chlorinating synthetic agents in the laboratory. The chloro-derivatives themselves are interesting since they represent a new class of substituted nitrogen chlorides which it has been our object to isolate. Besides the chloroderivatives of carbamic esters, the chloroderivatives of biuret and substituted biurets have been prepared.

It is very peculiar that no chloroderivative of the first ester of the series, *viz.*, methylcarbamic ester, could be prepared. It is, however, in keeping with the general notion that the first member of a homologous series behaves anomalously. The monochloroderivative of ethyl carbamic ester could be prepared by passing chlorine into a cold aqueous solution of the ester, as has been already described in a previous communication. In the case of ethylcarbamic ester, the monochloroderivative is the only product, however long the chlorination process is continued. But its next homolog behaves quite differently. Both monochloro- and dichloro-derivatives of propyl urethane could be obtained, although the latter could not be obtained pure, even when using chlorine in excess. The monochloroderivative could readily be prepared by passing a calculated quantity of chlorine into the aqueous solution of the urethane. Isobutyl carbamic ester can give rise to pure monochloroderivative although there is evidence of the formation of dichloroderivative, as is shown by the fact that the chlorine content approaches that of the dichloroderivative when chlorine is used in excess. In the case of the chlorination of isoamyl urethane, the monochloroderivative could not be prepared as an intermediate product, the dichloroderivative being formed at once.

Carbamic esters in which one or more amidic hydrogens are substituted, do not form the chloroderivatives at all. For instance, it has been found that chlorine has no action on chloral urethane. The action of chlorine on phenyl urethane is very peculiar, giving rise not to chloroderivatives, but to a complete condensation product. This might be accounted for by the fact that the phenyl radical, unlike the aliphatic radicals, easily takes part in condensation reactions. The action of chlorine on ethylidene ethyl carbamic ester is quite interesting. This breaks up during the chlorination process and dichloroethylcarbamic ester is the result, although the latter could not be prepared from ethyl carbamic ester itself under any conditions.

These compounds dissolve in almost all common organic solvents and are generally liquids of a pale yellow color. The boiling point, density and refractive index show a general regularity according to their increasing

molecular weights. The densities and refractive indices of the monochloroderivatives decrease while the boiling points increase with their increasing molecular weight.

The dichloroderivatives also show a similar behavior. On heating the liquids above their boiling points it was found that each had a temperature at which it decomposed with the separation of a solid product.

When these compounds are applied to the skin, a very painful sensation is produced and blisters are often formed which take considerable time to heal.

In the formation of these chloroderivatives substitution takes place with formation of hydrochloric acid, which remains dissolved in the mother liquor. As in other substituted nitrogen chlorides, the chlorine liberates iodine quantitatively from potassium iodide and this fact has been taken advantage of in analyzing these compounds.

Action of Chlorine on Methyl Carbamic Ester.

The action of chlorine on methyl urethane was studied under various conditions but in no case was it possible to isolate its corresponding chloroderivative. It appears that it is not capable of forming a chloroderivative.

Chlorine was first passed through a dilute solution of the ester, but even after passing it for a considerable time no sign of separation of the desired product was evident, although the peculiar smell belonging to this class of chloro compounds was perceived. It was thought that the great solubility of the chloroester might prevent its separation. To overcome this a saturated solution of methyl urethane was subjected to the prolonged action of chlorine, but in this case also, the solution only gave the peculiar smell due to chloroderivatives.

In order to determine whether the great solubility of the chloroderivative, together with the presence of the hydrochloric acid formed in the solution as a result of the reaction, prevented the reaction from proceeding beyond a limited extent the action of chlorine was next tried on the finely powdered urethane with only a few drops of water. The mass liquefied in a few minutes while the chlorine was passed into it. On examining the product, however, it was found that only a very small quantity of the substance was transformed into the chloroderivative. This causes the whole substance to liquefy and prevents further chlorination in accordance with the reason put forward above.

Finally it was decided to try the action of dry chlorine on the dry substance but no reaction took place. Nor was chlorination obtained when chlorine was passed into molten methyl urethane, the resulting product being unchanged methyl urethane.

Action of Chlorine on Propyl Urethane, Monochloropropylurethane, $\text{NHCl}-\text{CO}-\text{OC}_3\text{H}_7$.—The action of chlorine on propyl urethane results in formation of both monochloro- and dichloroderivatives, according as the

chlorination is stopped at an intermediate stage or carried to completion. An attempt was first made to prepare monochlorourethane by passing a rapid current of chlorine through a saturated aqueous solution of propyl urethane. Within a few minutes, a liquid began to separate. This was separated, dried and the halogen estimated. A much higher value than is required for the monochloroderivative was obtained. That the high percentage of chlorine was not due to chlorine dissolved in the liquid was shown by washing with water and dilute alkali which did not change the chlorine content. Hence, it was quite evident that the higher percentage of chlorine was due to the formation of some dichloroderivative. Since the liquid boils with decomposition, a separation could not be effected by distillation. Finally, the monochloroderivative was prepared by passing a calculated amount of chlorine into an aqueous solution of the substance, when the desired product separated as a pale yellow oil in the pure state.

0.2682 g. required 20.0 cc. 0.1 *N* thiosulfate; Cl as NaCl = 26.51.

0.2143 g. gave 0.2272 g. AgCl by Carius's method; Cl = 26.23.

0.1564 g. gave 0.1976 g. CO₂ and 0.0774 g. H₂O; C = 34.46; H = 5.49.

0.0974 g. gave 8.6 cc. N₂ at 30° and 760 mm.; N = 10.23.

Calc. for C₄H₈O₂NCl, C = 34.69; H = 5.83; N = 9.78; Cl = 25.82.

The substance is a pale yellow oil having, at 30°, a specific gravity of 1.269 and a refractive index of 1.45377. It is soluble in ether, methyl alcohol, ethyl alcohol, acetone, chloroform, carbon tetrachloride and benzene. With some of these solvents it is miscible in all proportions. Its action on the skin is a little less energetic than its lower homolog ethylchlorocarbamic ester. It takes a longer time for the first sensation of pain and the appearance of the blister on the skin. Its action on amines and acid amides is quite similar to that of its lower homolog. By its action both monochloro- and dichlorobenzylamines could be prepared from benzylamine, according as the one or the other be employed in excess. Benzamide was similarly chlorinated by means of it, with the production of the monochloroderivative.

Dichloropropylurethane, NCl₂—CO—OC₃H₇.—For the preparation of the dichloroderivative an excess of chlorine was passed through a well-cooled, saturated solution of the ester when it was obtained as a pale yellow mobile liquid. The product was washed and dried as usual.

0.2676 g. required 28.6 cc. 0.1 *N* thiosulfate; Cl as : NCl = 37.93; calc. for CC₄H₇NO₂Cl₂, Cl = 41.28.

As appears from the analysis above, the pure dichloroderivative could not be prepared. It is quite possible that during its formation in the presence of water, some of the monochloroderivative remains unchanged. Its properties are quite similar to the monochlorourethane as regards its solubility, action on amines and acid amides and action on the skin.

Monochloroisobutylurethane, $\text{NHCl}-\text{CO}-\text{OC}_4\text{H}_9$.—Like propylurethane, butyl urethane undergoes chlorination with the formation of both monochloro- and dichloroderivatives although the latter could not be prepared even in a state approaching purity. It is obtained as a mixture with the monochloroderivative. The monochloroderivative could be prepared similarly to monochloropropylurethane by passing a calculated amount of chlorine through a well-cooled aqueous solution of the urethane, when it separated as a pale yellow, mobile liquid having the characteristic odor of the chlorourethanes. It was washed and dried as usual.

0.1751 g. required 11.3 cc. 0.1 *N* thiosulfate; Cl as : $\text{NCl} = 22.84$. 0.2010 g. gave 0.1876 g. AgCl by Carius's method; Cl = 23.09. Calc. for $\text{NHCICO}-\text{OC}_4\text{H}_9$, Cl = 23.44.

The substance is a pale yellow, mobile liquid having a specific gravity of 1.156 and a refractive index of 1.44615 at 30° . The compound begins to boil with decomposition at 140° leaving off a white solid. At the same time white vapors are given out which condense on the upper and cooler parts of the tube. Its action on the skin is a little less energetic than its lower homolog and its behavior towards amines and acid amides is the same as that of its lower homologs, giving rise to chloroderivatives.

When a large excess of chlorine is used and the current is continued even after the separation of oil, there is a tendency for the formation of the dichloroderivative although it could not be obtained in a state of purity. It is obtained as a mixture of monochloro- and dichloroderivatives. In one experiment the percentage of chlorine went as high as 30.5%, the values calculated for monochloroderivative being 23.4 and that for the dichloroderivative 38.17%. As no method could be found to effect a separation the dichloroderivative could not be prepared in a pure state.

Dichloroisoamylurethane, $\text{NCl}_2-\text{CO}-\text{OC}_5\text{H}_{11}$.—The action of chlorine on isoamylcarbamate gives rise at once to the dichloroderivative and the monochloro product could not be obtained at all, even by stopping the chlorination process at an intermediate stage. For the preparation of the dichloroderivative a current of chlorine is passed into a quantity of powdered isoamylurethane suspended in water. The mother liquor, which at the beginning appears like a white emulsion, becomes quite clear after saturation with chlorine and the required product separates as a yellow oil. The oil was washed and dried as usual.

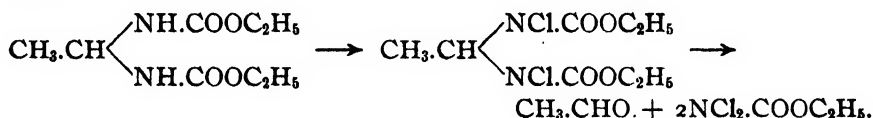
0.0957 g. required 9.45 cc. 0.1 *N* thiosulfate; Cl as : $\text{NCl} = 35.01$. Calc. for $\text{C}_5\text{H}_{11}\text{O}_2\text{NCl}_2$, Cl = 35.5.

The substance has a specific gravity of 1.156* and a refractive index of 1.45146 at 30° . It is soluble in ordinary solvents. Its action on the skin and on amines and acid amides is quite the same as that of its lower homologs. The compound begins to boil at 124° . At 145° dense white vapors arise from the surface of the liquid and the reaction is so vigorous

that it is accompanied by a sudden flash of light; at the same time a crystalline brown solid separates from the liquid.

Action of Chlorine on a Ethylideneurethane, Dichlorocarbamic Ester, $N-Cl_2.COOC_2H_5$.—The action of chlorine on ethylideneurethane is somewhat peculiar. It is a condensation product of acetaldehyde and ethyl urethane and it does not admit of chlorination before the rupture of the substance, and the rupture takes place with the formation of dichlorocarbamic ester, which could not be prepared by the direct action of chlorine on the ester as has been noted before.¹ Even by this method, the dichloroderivatives could not be prepared in a pure state being contaminated with a little monochloroderivative. The action which takes place may be explained thus: One atom of hydrogen directly united with nitrogen is

chlorinated first to form at $CH_3.CH \begin{cases} NCl.COOC_2H_5 \\ NCl.COOC_2H_5 \end{cases}$ but on further action of chlorine the compound breaks up into CH_3CHO and $NCl_2.COOC_2H_5$ thus:



For the preparation of the compound, ethylideneurethane was first powdered and suspended in water and then a rapid current of chlorine was passed through it. The solid gradually begins to change into oily globules which become more and more mobile and the whole of it finally changing into a mobile yellow oil when the action is complete. The liquid was separated from the mother liquor, washed and then dried. The yield amounted to about 60% of the theory.

0.1721 g. required 21 cc. 0.1 *N* thiosulfate; Cl as : $NCl_2.COOC_2H_5$, Cl = 44.93. Calc. for $NCl_2.COOC_2H_5$, Cl = 44.93.

The low percentage of chlorine in the product may be accounted for by the presence of monochloroderivative as impurity, from which it could not be separated.

It is a pale yellow, mobile liquid having at 30° a specific gravity of 1.304 and a refractive index of 1.45397. It has a smell similar to the ethylmonochlorocarbamic ester and affects the skin like the monochlorocarbamic ester. Its action on amines and acid amides is the same as has been found with the other members of the series, this being the most active among them. •

Action of Chlorine on Chloralurethane.—The action of chlorine on chloralurethane does not give rise to any chloroderivative. It appears that urethanes in which an amido group is substituted do not give chloro-

¹ *Loc. cit.*

derivatives unless they are decomposed into the original esters. In the case of ethylideneurethane it has been found that it decomposes into the original ester, the dichloroderivative of which is the result of the action of chlorine. But the stability of chlorourethane is considerable, owing to the electronegative character of the three chlorine atoms, and hence the compound remains unchanged on subjecting it to the action of chlorine under varying conditions.

Action of Chlorine on Phenylurethane.—The result of the action of chlorine on phenylurethane is quite interesting. Instead of giving rise to the usual chloroderivatives, a complex condensation product results. The first action might, no doubt, give rise to the usual chloroderivatives but the great reactivity of phenyl radical for substitution reactions might be the cause of the production of the condensation product.

A rather slow current of chlorine was passed through a quantity of phenylurethane suspended in water. At first a white emulsion came down which soon changed into a dirty gray, and then green, oily substance which afterwards turned to a pasty, brownish, solid mass. This was washed thoroughly with water and left to dry in a vacuum desiccator. The substance was first recrystallized from acetone and then again from ether. When crystals first form from an ethereal solution they appear perfectly white but after some time, and on keeping in a desiccator, they gradually turn to a very pale yellow color. On partially washing these crystals with successive small quantities of ether, white flakes of crystals remain behind. These crystals, on dissolving in alcohol and allowing to recrystallize undisturbed, give beautiful white needles. The substance had a sharp melting point of 83° . It is soluble in acetone, ether and alcohol. Its constitution could not be determined at present.

0.1321 g. gave 0.2102 g. CO_2 and 0.0520 H_2O , $\text{C} = 43.40$; $\text{H} = 4.00$. 0.1093 g. gave 7.8 cc. N_2 at 30° and 760 mm., $\text{N} = 8.10$. 0.1426 g. gave 0.0816 g. AgCl , $\text{Cl} = 14.16$. Calc. for $\text{C}_{18}\text{H}_{20}\text{N}_3\text{Cl}_2\text{O}_9$, $\text{C} = 43.72$; $\text{H} = 4.06$; $\text{N} = 8.50$; $\text{Cl} = 14.37$.

The Hydrolytic Product of Monochlorourethane.—It has been shown previously that monochlorourethane undergoes hydrolysis when kept in contact with water and alkalis for a time extending over several days in presence of air. The compound is completely decomposed and a white crystalline substance is formed below the water. The substance was recrystallized from alcohol and had a sharp melting point of 147° . Many preparations were undertaken with the same results. The compound corresponds to the formula $\text{C}_7\text{H}_{15}\text{N}_3\text{O}_4\text{Cl}$.

0.0940 g. gave 0.1188 CO_2 and 0.0528 H_2O , $\text{C} = 34.47$; $\text{H} = 6.18$. 0.1158 g. gave 17.00 cc. N_2 at 28.5° and 763 mm., $\text{N} = 17.20$. 0.0583 g. gave 0.0344 AgCl , $\text{Cl} = 14.50$. Calc. for $\text{C}_7\text{H}_{15}\text{N}_3\text{O}_4\text{Cl}$, $\text{C} = 34.92$; $\text{H} = 6.23$; $\text{N} = 17.46$; $\text{Cl} = 14.77$.

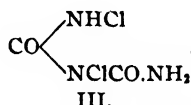
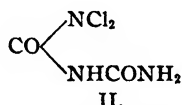
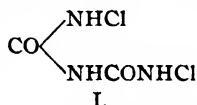
Its constitutional formula could not be assigned at present and further work is necessary to elucidate its constitution.

The hydrolytic products of the other chlorocarbamic esters are being studied and attempts are being made to apply them as synthetic agents.

The Action of Chlorine on Biuret and Substituted Biurets.

Having been successful in isolating the various chloroderivatives of the different carbamic esters, which are in fact substituted nitrogen chlorides, it was thought possible to substitute by chlorine the hydrogen atoms united to nitrogen in more complicated derivatives derived from carbamide in which the amido groups of urea remain intact, *viz.*, biuret and substituted biurets. From biurets, dichlorobiuret has been obtained, and acetylbiuret gave rise to dichloroacetylbiuret. These are important on account of the fact that they represent a new class of substituted nitrogen chlorides which have hitherto not been prepared.

Dichlorobiuret, $\text{NHCl}-\text{CO}-\text{NHCONHCl}$.—The action of chlorine on biuret gives rise to a dichloroderivative and there are three possible formulas for the same, *viz.*,



But on careful consideration and study of the other substituted nitrogen chlorides, it can be safely asserted that Formula I is the only possible one. The second formula can be rejected on the ground that both atoms of hydrogen of one of the NH_2 groups cannot be replaced when another symmetrically situated NH_2 group remains unacted upon. Formula III can also be rejected, owing to the improbability of substitution by chlorine in an imido group in preference to that in an amido group.

A few grams of biuret were taken in a flask with a quantity of water insufficient to dissolve the whole at the ordinary temperature. The water was next warmed to $60-70^\circ$ until all the biuret went into solution. When the solution had cooled somewhat, a rapid current of chlorine was passed through it when, within a very short time, a white precipitate began to form. This increased in quantity as the current of chlorine was continued. When it was found that the amount of precipitate no longer increased, the current of chlorine was stopped and the crystals obtained were filtered with suction and washed thoroughly with water. The substance thus obtained consisted of a crystalline white powder. It was then dissolved in alcohol and crystallized therefrom. The substance melted with decomposition at 160° with a sharp and sudden crackling sound.

0.1673 g. gave 0.8293 g. CO_2 and 0.0328 H_2O ; C = 13.52; H = 1.94. 0.0836 g. gave 17.8 cc. N_2 at 25°C . and 764 mm., N = 24.69. 0.1813 g. gave 0.3007 g. AgCl , Cl = 41.03. Calc. for $\text{C}_2\text{H}_3\text{O}_2\text{N}_3\text{Cl}_2$, C = 13.59; H = 1.74; N = 24.42; Cl = 41.28.

This substance, like the other substituted nitrogen chlorides, liberates

iodine from potassium iodide. Hence a volumetric estimation was undertaken in order to determine whether it agreed with the volumetric estimation given above. However, a certain anomaly was noticed which calls for a special explanation. The analysis was carried out by adding a weighed quantity of the biuret derivative to a solution of potassium iodide and then titrating the liberated iodine with sodium thiosulfate. The percentage of chlorine as the mean of several analyses was found to be 51.35%, whereas that obtained by gravimetric method was only 41.03. The chlorine calculated for trichlorobiuret is 51.55. The gravimetric estimation gives as a rule the whole of the chlorine of a substance if carried out in sealed tubes by the Carius method. Hence the excess of chlorine found by the volumetric method is certainly due to some decomposition reaction of dichlorobiuret itself which liberates an equivalent quantity of iodine from potassium iodide.¹

The action which takes place is one of substitution like the carbamides and carbamic esters, resulting in the liberation of hydrochloric acid which was found in the filtrate from the precipitated dichlorobiuret. The reaction is quantitative, unlike carbamide, since biuret is neutral and does not combine with hydrochloric acid, which therefore does not interfere with the chlorination.

The compound is quite stable, unlike the other substituted nitrogen chlorides which have a great tendency to decompose. A sample of the product was analyzed after being kept for nearly a month when all its chlorine was found intact although the substance could not be kept indefinitely. The compound was vigorously acted upon by a fairly strong solution of caustic potash but it dissolves to a yellow solution in a dilute solution of the same. It is fairly soluble in ether and insoluble in water and benzene.

Dichloroacetylbiuret, $\text{NHCO.CH}_3\text{—CO—NHCONCl}_2$. — Monoacetylbiuret was prepared according to the method of Schiff.² The monoacetylbiuret is dissolved in a small quantity of water by heating on the water bath to make a saturated solution. After cooling the solution to some extent, a rapid current of chlorine was passed into it when, within a few minutes, crystals began to appear. After passing chlorine for some time longer the solid was filtered off and washed with water in which it seemed to be slightly soluble. It is purified by crystallization from alcohol. The pure product melts with decomposition at 170° with a sharp crackling sound similar to that given by dichlorobiuret.

¹ The author has apparently overlooked the fact that compounds of the type of nitrogen trichloride liberate two atoms of iodine for each atom of chlorine present. See Hentschel, *Ber.*, 30, 1434. This is evidently because the chlorine is *positive* in these compounds. Noyes and Lyon, *THIS JOURNAL*, 23, 462 (1901); Noyes, *Ibid.*, 35, 767 (1913).—EDITOR.

² *Ann.*, 291, 377 (1896).

0.1380 g. required 13 cc. 0.1 *N* thiosulfate; Cl as : NCl = 33.31. 0.0933 g. gave 12.2 cc. N_2 at 29.8° and 763 mm., N = 19.80. 0.1701 g. gave 0.1387 g. CO_2 and 0.0379 g. H_2O , C = 22.24; H = 2.34. Calc. for $C_7H_5O_2N_3Cl$: C = 22.43; H = 2.34; N = 19.62; Cl = 33.31.

All attempts to prepare the chloroderivative of benzoylbiuret were unsuccessful. It appears that the increment of the acidic nature of the substance by a substitution of the benzoyl group has interfered with the formation of the chloroderivative.

The chloroderivative of other substituted biurets are in the course of preparation, as also other substituted nitrogen chlorides.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

CONTRIBUTIONS TO THE KNOWLEDGE OF HALOGENATION.

VIII. NEW SERIES OF CHLOROHYDROXY COMPOUNDS.

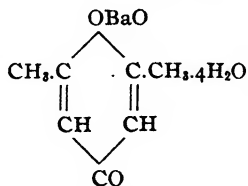
THE HYDROLYTIC CHLORINATION OF DIMETHYL- PYRONE. THE ISOLATION OF 2,6-DICHLORO- HYDROXY-3,5-DICHLORO-4-KETOHEPTANE AND ITS DECOMPOSITION INTO 3,5- DICHLORO-2,4,6-TRIOXYHEPTANE.

By RASIK LAL DATTA AND SATYARANJAN DAS GUPTA.

Received January 12, 1915.

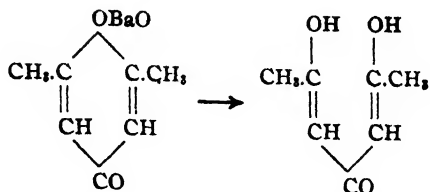
The chlorination of dimethylpyrone has been effected by a variety of reagents. Chlorine has been found quite satisfactory to effect the change, although potassium chlorate and hydrochloric acid and also aqua regia, which give chlorine in the nascent state, can effect the chlorination of dimethylpyrone with the taking up of a water molecule and the opening of the pyrone ring.

The action of barium hydrate on 2,6-dimethylpyrone¹ presents a close analogy to the case in question. When an aqueous solution of dimethylpyrone is boiled with baryta water, there separates an insoluble barium salt, containing four molecules of water of crystallization,

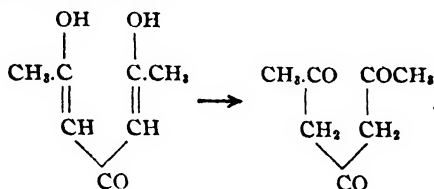


When this salt is dissolved in hydrochloric acid and the resulting solution is extracted with ether, diacetylacetone is formed. By the removal of barium as barium chloride, the hypothetical dihydroxy compound is first formed, thus:

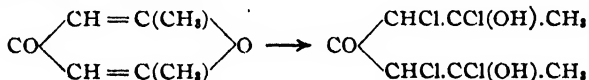
¹ Feist, *Ann.*, 257, 276 (1890).



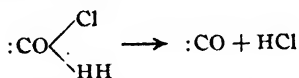
But according to Erlenmeyer's rule¹ free hydroxyl cannot exist as such, it rearranges itself, the oxygen of the hydroxyl unites doubly with carbon and, as a result of such molecular rearrangement, diacetylacetone or 2,4,6-triketoheptane is produced.



When dimethylpyrone is subjected to the action of chlorine, potassium chlorate and hydrochloric acid and also aqua regia, the compound becomes chlorinated, first four atoms of chlorine attach themselves to the two unsaturated double bonds and, secondly, the pyrone ring opens up, taking a water molecule thus:



Unlike the hydrolytic product from dimethylpyrone itself, the hydroxyl groups are on the doubly united carbon atoms, hence they remain as such, yielding a compound of a new type and remarkable interest. The compound so formed has been found to be 2,6-dichlorohydroxy-3,5-dichloro-4-ketoheptane. In this compound, a chlorine atom and a hydroxyl group are both united with the same carbon atom. The above compound is very unstable, as might be easily inferred from the nature of the groups attached. The attempts at preparing such types of compounds by direct chlorination of compounds containing hydroxyl group have hitherto been a failure, since there is a strong tendency for the splitting off of hydrochloric acid according to the following scheme:

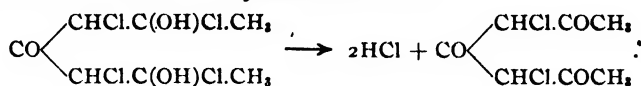


But the formation of such a compound is possible in the case in question by the addition of chlorine atoms to the unsaturated bonds and the simultaneous taking up of water molecule without any side reaction.

As can be well anticipated from the nature of the groups attached,

¹ Ber., 13, 309 (1880); 25, 1781 (1892).

such a compound would readily lose hydrochloric acid and this has been found to be the case. When the compound, which is a fairly viscous oil, was kept in a stoppered bottle, its viscosity diminished in a few days and fumes of hydrochloric acid could be detected with ammonia vapor. The decomposed oil, on treatment with water, gives a white solid which has the formula $\text{CO}(\text{CHClCOCH}_3)_2$, which is 3,5-dichloro-2,4,6-triketone or dichlorodiacetylacetone and is formed from the original substance with the loss of two molecules of hydrochloric acid.



As by the direct hydrolysis of 2,6-dimethylpyrone we get diacetylacetone, so by the simultaneous chlorination and hydrolysis of 2,6-dimethylpyrone and subsequent hydrolysis of the resulting compound, dichlorodiacetylacetone has been prepared, which is a dichloroderivative of a triketone and it is interesting on account of the fact that similar chloroderivatives have not hitherto been prepared.

(1). **Preparation of 2,6-Dichlorohydroxy-3,5-dichloro-4-ketoheptane.**

(a) **From Chlorine.**—When chlorine is passed to an aqueous solution of dimethylpyrone, the compound separates as a pale yellow oil which could be separated, washed and dried as usual. The yield obtained was nearly quantitative.

(b) **From Potassium Chlorate and Hydrochloric Acid.**—Potassium chlorate and hydrochloric acid acts primarily as a chlorinating and oxidizing reagent; but in this case it acts purely as a chlorinating agent. The best yield of the substance is obtained when the following directions are carried out: Dimethylpyrone is dissolved in an excess of dilute hydrochloric acid (1 : 1) and potassium chlorate in fine crystals is added in small quantities, when it dissolves without any evolution of gas. Repeated shaking with further quantities of potassium chlorate results in its solution, the solution turning yellowish. If the test tube be left to itself, the color appears after a considerable time but if briskly shaken it appears in about fifteen minutes. At the same time a peculiar odor is noticed. When more strong hydrochloric acid is added an immediate haziness is produced, which collects to a colorless oil. The direct precipitation of the oil points to the fact that it is insoluble in water in the presence of hydrochloric acid. After allowing the mixture to stand for some time the pale yellow oil which now collects at the bottom is separated by a separating funnel, washed with small quantities of water and dried by keeping in a desiccator.

The yield obtained is nearly theoretical.

Having no regard to the yield, the oil can be most rapidly prepared thus: Dimethylpyrone is dissolved in excess of strong hydrochloric acid (sp. gr.

1.16) and to it solid specks of potassium chlorate are gradually added with shaking, no second batch being added until the first batch dissolves. Turbidity results almost immediately and more and more of the oil collects. When no further turbidity is produced the addition of potassium chlorate is stopped. The oil can be separated and dried as usual.

(c) **From Aqua Regia.**—The action of aqua regia has been found to be destructive in almost all cases, except in the case of hydrocarbons, where it acts as a simple chlorinating agent¹ chiefly owing to the resisting power of the hydrocarbons. But it is very peculiar that this reagent acts simply as a chlorinating agent to form this substance which is so unstable. Dimethylpyrone is chlorinated quantitatively if the reaction is allowed to take place in the cold, whereas if the reaction be carried out at a slightly higher temperature, the product is a mixture of the chloroderivative and chloropicrin. Again, if the reaction is carried out at 100° pure chloropicrin, which is generally a product of the action of aqua regia on organic bodies, is produced.

For the preparation of the compound, dimethylpyrone in powder is gradually added to a mixture of nitric and hydrochloric acids, the latter being kept cold, preferably by immersion in cold water. Gradually the oil separates, increasing with continued addition of dimethylpyrone. The addition of dimethylpyrone is stopped when no more of the oil separates. The oil is next separated, washed and dried.

0.1824 g. gave 0.1908 g. CO₂ and 0.0417 g. H₂O, C = 28.52; H = 2.54. 0.0733 g. gave 0.1497 g. AgCl, Cl = 50.49. Calc. for C₇H₁₀O₃Cl₄, C = 29.58; H = 3.54; Cl = 50.00.

The substance is a pale yellow, moderately viscous oil which on heating first turns brown, then deep brown, finally leaving a black charred mass behind. The substance slowly decomposes on keeping, with the evolution of hydrochloric acid and a considerable diminution in the viscosity of the oil.

(2). Preparation of 3,5-Dichloro-2,4,6-triketoheptane.

A quantity of the oil which had been kept for some time in a stoppered bottle and whose viscosity had diminished considerably, was heated on the water bath for some time in order to remove any free hydrochloric acid which might be present. The halogen of the resulting oil was determined to ascertain its probable composition,

0.1458 g. gave 0.2914 g. AgCl, Cl = 48.56. Calc. for C₇H₁₀O₃Cl₄, Cl = 50.00.

The nearly equivalent chlorine content of this oil with that of the original oil led us to suspect that although the substance had decomposed into hydrochloric acid yet it might be in a mechanical mixture with the oil. In order to wash out the hydrochloric acid formed, the oil was repeatedly washed with water, when it became more and more viscous,

¹ Datta and Fernandes, *THIS JOURNAL*, 36, 1007 (1914).

finally showing signs of crystallization. The oil was left under water for some days to allow its crystallization to become complete. The substance was obtained in colorless crystals having a melting point of 145–146°. It was analyzed and was found to be 3,5-dichloro-2,4,6-trichloroheptane.

0.187 g. gave 0.2708 g. CO₂ and 0.0551 g. H₂O. C = 59.58; H = 3.40. 0.2331 g. gave 0.3157 AgCl, Cl = 33.65. H = 3.79; Cl = 33.65.

Further investigations on similar lines are being continued.

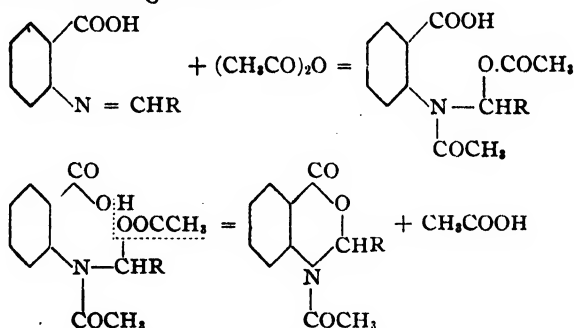
CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO.]
THE ACTION OF ACETIC ANHYDRIDE ON SOME BENZYLIDENE ANTHRANILIC ACIDS. IV.

By JOHN B. EKELEY AND CHARLES F. POE.

Received January 14, 1915.

Eighteen members of a series of acetketodihydrobenzmetoxazines have been described in previous papers.¹ These were obtained by the action of acetic anhydride upon the corresponding benzylidene anthranilic acids, according to the following reactions:



The previous members of this series, as described, were made by heating the benzylidene anthranilic acid with excess of acetic anhydride on the water bath for several hours, then evaporating off the excess of anhydride, and allowing the benzmetoxazine to crystallize out of the cooled concentrated solution. This method failed with certain benzylidene anthranilic acids, notably those derived from anisaldehyde and from piperonal, acetanthranilic acid being obtained instead of the expected benzmetoxazine. By a variation of the method, these benzmetoxazines have also been prepared. The benzylidene anthranilic acid was heated with molecular proportions of acetic anhydride in xylol solution for several hours, the excess of xylol was then distilled off, and the solution cooled in ice water. The benzmetoxazine derivative then crystallized out in a very

¹ THIS JOURNAL, 34, 161; 35, 282; 36, 604.

pure condition. The yield was much greater than had been obtained by the previous method of heating the two substances together without a solvent. Thus from 66 g. of benzylidene anthranilic acid 70 g. of phenylacetketodihydrobenzmetoxazine were obtained, whereas theory required 78 g. It was found, however, that in some cases the first method gives better results; for instance, in the case of salicylidene anthranilic acid, the latter method gives a syrupy mass from which it is difficult to obtain the benzmetoxazine, while by heating the benzylidene anthranilic acid directly with an excess of anhydride the benzmetoxazine is obtained easily and with a very satisfactory yield.

This paper will describe the benzylidene anthranilic acids obtained from *o*-toluylaldehyde, dibromosalicylaldehyde, 1,4- α -naphtholaldehyde, anisaldehyde, piperonal, methylvanillin, and *m*-methoxysalicylaldehyde, and the benzmetoxazine derivatives obtained from them.

In the condensation products from dibromosalicylaldehyde and from 1,4- α -naphtholaldehyde, it was found that the hydrogen of the hydroxyl group had been replaced by acetyl.

Experimental Part.

***o*-Toluylideneanthranilic Acid.**—Molecular amounts of *o*-toluylaldehyde and anthranilic acid in concentrated alcohol solution give a white, crystalline mass on standing, which may be recrystallized from a small amount of alcohol. Difficultly soluble in the ordinary organic solvents except methyl and ethyl alcohols, in which it is very soluble, and xylol. *M. p.* 143°.

Calc. for $C_{18}H_{13}O_2N$: N, 5.57; found: N, 5.6.

***o*-Methylphenylacetketodihydrobenzmetoxazine.** — *o*-Toluylideneanthranilic acid was heated with acetic anhydride in excess on the water bath for three hours. The excess acetic anhydride was then evaporated off, a stream of air being drawn over the liquid as it was being heated on the water bath. On cooling, the benzmetoxazine crystallized out. Recrystallized from alcohol it gave colorless prisms. Soluble in the ordinary organic solvents except ether. *M. p.* 166°.

Calc. for $C_{17}H_{15}O_2N$: N, 4.98; found: N, 4.9.

Dibromosalicylideneanthranilic Acid.—Dibromosalicylideneanthranilic acid separates out as a red crystalline mass when molecular amounts of dibromosalicylaldehyde and anthranilic acid are mixed in a cold alcohol solution. Recrystallized from alcohol, it yields scarlet needles, soluble in the ordinary organic solvents. *M. p.* 176°.

Calc. for $C_{14}H_9NBr_2$: N, 3.51; found: N, 3.22.

Acetyldibromophenylacetketodihydrobenzmetoxazine.—After heating dibromosalicylideneanthranilic acid with an excess of acetic anhydride and evaporating off the excess of anhydride as before, the benzmetoxazine

was obtained, mixed with a small amount of an intensely yellow crystalline substance, which probably is the unacetylated metoxazine. Colorless prisms, soluble in the ordinary organic solvents, except ether. M. p. 153°.

Calc. for $C_{18}H_{13}O_6NBr_2$: N, 2.89; found, N, 2.87.

Dibromophenylacetketodihydrobenzmetoxazine.—The yellow crystals remaining behind after heating the compound just described with alcohol, were recrystallized from boiling xylol, giving yellow needles, insoluble in most organic solvents. M. p. 274°.

Calc. for $C_{16}H_{11}O_4NBr_2$: N, 3.22; found: N, 3.17.

1,4- α -Naphtholideneanthranilic Acid.—Molecular amounts of α -1,4-naphtholaldehyde and anthranilic acid mixed in cold alcohol solution gave in a short time a maroon-colored mass. This was recrystallized from *warm* nitrobenzol, giving maroon-colored microscopic needles. Insoluble in the ordinary organic media, except acetone, methyl and ethyl alcohols. When boiled with nitrobenzol it decomposes partially. M. p. 195°.

Calc. for $C_{18}H_{13}O_3N$: N, 4.81; found: N, 5.04.

Acetyl - α - hydroxy - 1,4 - naphthoacetketodihydrobenzmetoxazine. — Heated on the water bath with excess acetic anhydride, 1,4- α -naphtholideneanthranilic acid yields the corresponding benzmetoxazine, the hydroxyl group being at the same time acetylated. Soluble in the ordinary organic solvents, difficultly in alcohol, from which it was recrystallized. Colorless microscopic needles. M. p. 238°.

Calc. for $C_{22}H_{17}O_6N$: N, 3.72; found, N, 3.57.

Anisylideneanthranilic Acid.—This was obtained as before by mixing a cold concentrated solution of anthranilic acid with anisaldehyde. The yellow crystals thus obtained were recrystallized from alcohol. Soluble in the ordinary organic solvents, except ether. M. p. 146°.

Calc. for $C_{15}H_{13}O_3N$: N, 5.49; found: N, 5.39.

***p* - Methoxyphenylacetketodihydrobenzmetoxazine.** — Molecular amounts of anisylideneanthranilic acid and acetic anhydride were heated for two and one half hours in xylol solution under reflux. The greater portion of the xylol was then distilled off and the remaining solution cooled in ice water. Sandy, colorless crystals separated out. These were filtered under suction, and, when washed with ether on the filter, were found to be snow-white in appearance. Soluble in the ordinary organic solvents except ether. M. p. 118°.

Calc. for $C_{17}H_{15}O_4N$: N, 4.70; found: N, 4.55.

Piperonalideneanthranilic Acid.—When molecular amounts of piperonal and anthranilic acid were brought together in cold alcohol solution, piperonalideneanthranilic acid separated out in a crystalline mass. Recrystallized from chloroform, it gave yellow crystals, soluble in the ordinary organic solvents except ether. M. p. 196°.

Calc. for $C_{18}H_{11}O_4N$: N, 5.20; found, N, 5.15.

3,4 - Methylene-dihydroxyphenylacetketodihydrobenzmetoxazine. — Molecular amounts of piperonalideneanthranilic acid and acetic anhydride were heated together in xylol solution under reflux for two hours. The greater portion of the xylol was then distilled off and the remaining solution cooled in ice water. The solution separated into two layers, the lower one thick and syrupy. After standing several hours, this solidified into a mass of crystals. These were filtered under suction and washed with ether on the filter, yielding sandy, white crystals of the expected benzmetoxazine. Soluble in the ordinary organic solvents except ether. M. p. 126° .

Calc. for $C_{17}H_{13}O_4N$: N, 4.50; found: N, 4.31.

Methylvanillylideneanthranilic Acid.—Molecular amounts of methyl vanillin and anthranilic acid were brought into concentrated cold alcoholic solution. After standing over night, the methylvanillylidene anthranilic acid appeared as bright yellow needles. These, recrystallized from xylol, were soluble in the ordinary organic solvents except ether. M. p. 163° .

Calc. for $C_{18}H_{16}O_4N$: N, 4.91; found: N, 4.76.

3,4-Dimethoxyphenylacetketodihydrobenzmetoxazine.—As in the two preceding cases, the benzmetoxazine was obtained by heating molecular amounts of the acid and acetic anhydride in xylol solution under reflux, distilling off most of the xylol, and cooling the remaining solution in ice water. The oil which separated out in this case would not crystallize until a small amount of alcohol had been added, whereupon the expected benzmetoxazine separated out as white sandy crystals. These were filtered off under suction, and washed with ether on the filter. Soluble in the ordinary organic solvents, except ether. M. p. 106° .

Calc. for $C_{18}H_{17}O_5N$: N, 4.28; found: N, 3.99.

***m*-Methoxysalicylideneanthranilic Acid.**—This acid is formed when molecular quantities of *m*-methoxysalicylaldehyde and anthranilic acid are heated in xylol solution for several hours under reflux. On standing the solution deposits red needles. These were recrystallized from chloroform. Soluble in the ordinary organic solvents. M. p. 113° .

Calc. for $C_{16}H_{13}O_5N$: N, 5.16; found: N, 4.80.

Acetyl-2-hydroxy-4-methoxyphenylacetketodihydrobenzmetoxazine.—Molecular proportions of *m*-methoxysalicylideneanthranilic acid and acetic anhydride heated in xylol solution as in previous cases yield colorless crystals of the acetylated oxazine after the concentrated solution has stood in the cold for several days. These were recrystallized from xylol. M. p. 187° .

Calc. for $C_{19}H_{17}O_6N$: N, 3.97; found: N, 3.76.

3-Methoxy-4-acetoxyphenylacetketodihydrobenzmetoxazine. — The preparation of the benzmetoxazine derived from vanillylideneanthranilic

acid and acetic anhydride by the method of heating the two substances in xylol under reflux gave a product which differed in its properties from that described in a previous paper¹ as made by the method of heating the acid and the acetic anhydride in excess. It is evident that the product previously described was not pure. To prepare the pure compound, it is necessary to heat the vanillylideneanthranilic acid with two molecular proportions of acetic anhydride in xylol solution under reflux for one hour. After distilling off the greater portion of the xylol, the acetylated metoxazine separates out on cooling in colorless sandy crystals. Recrystallized from xylol. Soluble in the ordinary organic solvents, except ether. M. p. 141°.

Calc. for $C_{18}H_{17}O_6N$: N, 3.97; found: N, 3.61.

BOULDER, COLORADO.

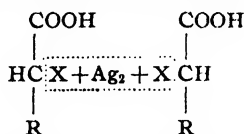
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN.]

THE ACTION OF FINELY DIVIDED SILVER ON α -BROMO- AND α -IODOPALMITIC ACIDS: SYNTHESIS OF TWO ISOMERIC DITETRADECYLSUCCINIC ACIDS.

By D. BREESE JONES.

Received January 12, 1915.

As is well known, the reaction between finely divided silver, so called "molecular silver", and monohalogen substitution products of the fatty acids is by no means a simple one. Besides the removal of halogen from two molecules of the substituted fatty acid and union taking place through the released affinities of the carbon atoms with formation of dibasic acids,



there are always formed several other products of the reaction. Hell and his co-workers have studied the action of silver on several halogen substituted fatty acids. From ethyl α -bromoisobutyrate and silver² were obtained two isomeric tetramethylsuccinic acids, carbon dioxide, ethyl bromide, isobutyric acid and methylacrylic acid, while ethyl α -bromobutyrate³ yielded ethyl bromide, ethyl alcohol, ethyl butyrate, two diethylsuccinic acids, and a sirup whose composition agrees with that of hydroxysuberic acid. Ethyl α -bromoisovalerianate with silver⁴ yielded two isomeric sebacic acids, ethyl bromide, ethyl isovalerianate, and

¹ THIS JOURNAL, 35, 164 (1913).

² Hell, *Ber.*, 10, 2229 (1877).

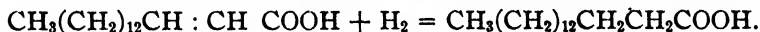
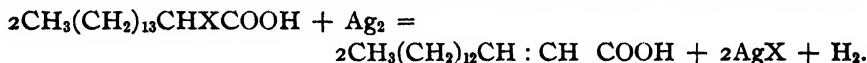
³ Hell and Mühlhäuser, *Ibid.*, 13, 473-9 (1880).

⁴ Hell and Mayer, *Ibid.*, 22, 48 (1888).

polymeric dimethylacrylic acids. Likewise ethyl α -bromopropionate¹ gave two dimethylsuccinic acids, ethyl propionate, ethyl acrylate and pyrocinchonic acid. In practically all cases two isomeric dialkylsuccinic acids were obtained.

It was accordingly deemed of interest to investigate the action of silver on halogen derivatives of higher fatty acids. In this article is described the action of silver on α -bromo-, and iodopalmitic acids. It was found that the halogen is readily removed from both bromo-, and iodopalmitic acid, either by heating alone with silver at a temperature of 130 to 140°, or by boiling the mixture in heptane. Among the products of the reaction, were obtained palmitic acid, an oil which showed properties of unsaturation, and the heretofore unknown two isomeric ditetradecylsuccinic acids.

Palmitic acid was invariably found as a product of the reaction. In one experiment with bromopalmitic acid, it comprised at least 20% of the original bromo acid taken, while in another experiment with iodopalmitic acid, 13% of the latter was converted into palmitic acid. This reduction of the original halogen acid probably takes place by abstraction of the halhydric acid, and subsequent reduction of the unsaturated acid.



The identification of the unsaturated acid, which is a constituent of the oily product which was always obtained, could not be determined, because of the small amount available to work with. Other unsaturated compounds than 1,2-hexadecylenic acid, might also well be present. Many olefines readily polymerize, with the formation of compounds which are still unsaturated. Hell and Mayer² obtained polymeric dimethylacrylic acid by action of silver on ethyl bromoisovalerianate. That an unsaturated dibasic acid of the type (I) may also be formed, is shown by the formation of pyrocinchonic acid (II) from bromopropionic acid and silver³



The two isomeric ditetradecylsuccinic acids obtained by action of silver on bromo-, and iodopalmitic acids, are characterized by difference in solubility and melting points. One melts at 135 to 136°, and is extremely difficultly soluble in most organic solvents, while the other melts at 95 to 96°, and is moderately soluble. When heated to about 170°,

¹ Hell and Rothberg, *Ber.*, **22**, 64 (1888).

² *Loc. cit.*

³ Hell and Rothberg, *Loc. cit.*

the acid melting at 135° loses water, and is converted into an anhydride melting at 45 to 45.5° , which on hydrolysis yields the acid melting at 95° . This latter acid, on the other hand, when heated to about 150° , also loses water and is converted into an unstable anhydride, which readily transforms into the same anhydride as that obtained by heating the higher melting acid. The acid melting at 135° was formed in much the larger amount of the two, although the yield was small. The maximum yield of this acid obtained from bromopalmitic acid was 8% of the amount calculated, while a maximum yield of 13% was obtained from iodopalmitic acid. The yield was better when the constituents were boiled in heptane, than when heated alone.

Practically all of the known symmetrically substituted dialkylsuccinic acids occur in two isomeric forms, which are characterized by a considerable difference in solubility and melting point. The nature of the isomerism has been long a question of speculation. These isomers have been commonly referred to as the "fumaroid" and "maleinoid" forms. According to van't Hoff's theory, these compounds having two asymmetric carbon atoms, would be naturally expected to occur in two inactive isomeric modifications, one inactive because of external, and the other inactive because of internal compensation, as in the case of *racemic*, and *meso* tartaric acids. Furthermore, on account of the many analogies they offer with the tartaric acids, their isomerism has frequently been referred to as of the same type. Accordingly, the fumaroid form, being the less soluble and having the higher melting point, was looked upon as having the *racemic*, and the maleinoid, as having the *meso* structure. However, this assumption was considered doubtful, as no one of the inactive dialkylsuccinic acids had ever been resolved into its active components, and not all of their properties fitted in with the analogy of the tartaric acids.¹ Bischoff,² to account for this isomerism, advanced a theory of *dynamical isomerism*, in which he considered the equilibrium positions of the atoms and radicals joined to the two asymmetric carbon atoms.

It is rather remarkable that it was not until 1913, that one of the inactive dialkylsuccinic acids was for the first time resolved into its optically active antipodes, when Werner and Basyrin³ succeeded in resolving one of the two inactive forms of dimethylsuccinic acid. Noyes and Kyriakides⁴ have also recently resolved into its optically active forms, one of the two inactive isomeric α, α' -dimethyladipic acids. It is very significant that in both of these cases, it was the more soluble acid, and the one having the lower melting point which was decomposed into the optically

¹ Auwers, *Ann.*, 309, 316 (1899).

² Bischoff, *Ber.*, 24, 1074, 1085.

³ Werner and Basyrin, *Ber.*, 46, 3229 (1913).

⁴ Noyes and Kyriakides, *THIS JOURNAL*, 32, 1057 (1910).

active components. It was found impossible to resolve the less soluble acid having the higher melting point. From this it appears that, unlike the tartaric acids, the racemic, or fumaroid form of the dialkylsuccinic acids are the varieties of the low, and not of the high melting points.

It is extremely probable, therefore, that of the two ditetradecylsuccinic acids described in this article, the less soluble one melting at 135 to 136° is the *meso*, while the more soluble acid melting at 95° is the *racemic* modification.

Experimental.

The palmitic acid, which was used in this work for the preparation of the bromo- and iodopalmitic acid, was obtained by saponification of palm oil with potassium hydroxide and decomposition of the resulting soap with hydrochloric acid. It was fractionally distilled at 35 – 45 mm. The fraction boiling at 240 – 250° after two recrystallizations from gasoline was practically pure. It melted at 61.5° to 62° .

α -Bromopalmitic acid was prepared according to Hell and Jordanoff's¹ method by adding dry bromine to a mixture of palmitic acid and red phosphorus. An excess of bromine (40 cc.), which had been previously dried with concentrated sulfuric acid, was slowly dropped onto a mixture of 75 g. of palmitic acid which was intimately mixed with 3.5 g. of red phosphorus. The reaction was carried on in the sunlight and at first was violent, the addition of every drop of bromine being attended with a flash. After most of the bromine had been added the mixture was heated on a boiling water bath until the fumes of hydrobromic acid had practically ceased. The excess of bromine was removed by drawing a current of air through the warm mixture for a few minutes. The reddish, oily product was then poured into about a liter of water, allowed to stand over night, extracted with petroleum ether, and the acid allowed to crystallize by spontaneous evaporation of the solvent. No marked reaction was observed when the oily product was poured into the cold water. (Hell records that a vigorous reaction with evolution of heat occurs at this stage.) After a few recrystallizations from petroleum ether or ligroin the bromopalmitic acid separates in clusters of prisms which melt at 53 to 53.5° . The yield of the purified acid was 40 g.

Iodopalmitic acid was prepared by boiling for three hours 95 g. of bromopalmitic acid, dissolved in 200 cc. of alcohol, with 70 g. of potassium iodide. After filtering off the potassium bromide, the straw-colored filtrate was evaporated nearly to dryness and the residue triturated several times with potassium iodide solution, to remove free iodine. The iodopalmitic acid crystallized from petroleum ether in glistening scales which melted at 60 to 61° . (Ponizio² gives 57° .) Obtained a yield of 90 g.

¹ Hell and Jordanoff, *Ber.*, 24, 938 (1891).

² Ponizio, *Chem. Zentr.*, 82, 1361 (1911).

Action of Silver on α -Bromopalmitic Acid.—Three g. of bromopalmitic acid, dissolved in 25 cc. of heptane, was boiled with 3.1 g. of finely divided silver for nine hours in a paraffin bath. The silver was prepared by reduction of silver chloride by glucose and sodium hydroxide, and then dried at 135 to 140°. Evidence of a reaction between the silver and bromopalmitic acid was apparent within half an hour, as indicated by a change in the color and texture of the silver residue. The temperature of the boiling mixture was about 115°. The silver residue was filtered from the hot solution, and the filtrate was evaporated on a water bath to a small volume of liquid which solidified on cooling. This was then warmed with several times its volume of petroleum ether, allowed to stand for a few minutes, and the portion which remained undissolved filtered off. This white substance, which amounted to 0.08 g., melted at 120–130° to a clear oil and decomposed at 165–170° with evolution of bubbles.

The silver residue which had been filtered off, was first washed with hot petroleum ether, then extracted with boiling alcohol, and the alcoholic extract evaporated to dryness. This residue was now warmed with petroleum ether to remove traces of soluble matter, and 0.12 g. of a hard, light-colored, pulverulent substance was filtered off, which melted at 131–133° to a clear oil and decomposed with gradual effervescence at 155–160°. Altogether, there was thus obtained of this high melting product, 0.2 g., or 8% of the theoretical yield calculated for ditetradecylsuccinic acid.

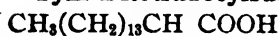
The original heptane filtrate, to which was added the petroleum ether washings of the silver residue, yielded on evaporation an oil, which on cooling partially solidified forming a pasty mixture. This was stirred with ice-cold petroleum ether and filtered. By this method, 0.9 g. of a crystalline substance was separated from the oily fraction. This substance is soluble in dilute alkalis, from which it can be reprecipitated by addition of acids. After two recrystallizations from dilute alcohol, it separated in fine needles which melted sharply at 62–63°. Some of this substance mixed with pure palmitic acid melting at 62.5°, caused no lowering of the melting point, showing it to be pure palmitic acid. There was obtained 0.6 g. of this acid, which is 20% of the bromopalmitic acid originally taken. The actual percentage of palmitic acid formed is doubtless considerably more, as some must have been lost during the purification.

The petroleum ether filtrate from the palmitic acid left on evaporation a straw-colored oil. The examination of this sirupy product of the reaction is described in a subsequent paragraph.

Action of Silver on α -Iodopalmitic Acid.—The action of silver on iodopalmitic acid was carried on under the same conditions as in the case of bromopalmitic acid. The results obtained were analogous, excepting that a larger yield of the high melting acid, and a smaller amount of palmitic

acid were obtained. In one experiment 13% of the calculated yield of the former was obtained, while 13.3% of the iodo acid was converted into palmitic acid. These results suggest that iodopalmitic acid has a less tendency than the bromo acid, to split off halhydric acid, with consequently a smaller reduction to palmitic acid, and a greater tendency to lose its halogen, with the formation of the high melting acid.

Sym-Ditetradecylsuccinic Acid (melting at $135-6^{\circ}$),



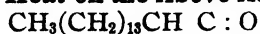
$\text{CH}_3(\text{CH}_2)_{13}\text{CH COOH}$.—All of the fractions of the high melting acid,

(melting at $130-133^{\circ}$), obtained from several preparations as described above, were united and dissolved in boiling alcohol. On standing there soon separated from the alcoholic solution hard granular nodules, which melted to a clear oil at $133-135^{\circ}$, and decomposed at $170-180^{\circ}$ with slow evolution of gas, leaving a clear, colorless oil. After one or two recrystallizations from alcohol, the substance was obtained in hard clusters, or rosetts, which melted sharply at $134-135^{\circ}$. It can also be crystallized from hot glacial acetic acid, in the form of fine, soft aggregates which, when dry, can readily be reduced to a fine, flour-like powder.

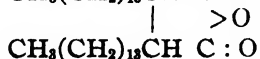
Calc. for $\text{C}_{32}\text{H}_{62}\text{O}_4$: C, 75.29; H, 12.16. Found: C, 74.93, 74.83; H, 12.07, 11.96.

It slowly dissolves in boiling dilute ammonium hydroxide, forming a slightly opalescent solution, which, when acidified with dilute hydrochloric acid, regenerates the free acid as a light flocculent precipitate, melting at $135-136^{\circ}$. This acid is characterized by being extremely difficultly soluble in most solvents. It is practically insoluble in water, chloroform, acetone, carbon tetrachloride, ether, petroleum ether, benzene and ethyl acetate. It is moderately soluble in hot, but very sparingly soluble in cold alcohol. It dissolves readily in hot glacial acetic acid, but separates out again almost quantitatively on cooling. On account of these properties some trouble was encountered in purifying it. It can be best purified by dissolving in warm dilute ammonium hydroxide, precipitating with dilute hydrochloric acid and recrystallizing, first from alcohol and then from acetic acid. Thus purified it melts at $135-136^{\circ}$, and decomposes with bubbling at $165-170^{\circ}$.

Action of Heat on the Above Acid. Formation of Ditetradecylsuccinic



Anhydride,



—The ditetradecylsuccinic acid, contained in a short test tube, was heated to 180° in a sulfuric acid bath, and maintained at that temperature until the formation of bubbles had largely subsided. The temperature was finally raised to about 200° , at which point the evolution of gas had entirely ceased. During the heating, which occupied about three-quarters of an hour, the substance was stirred

with a platinum wire. The thick, slightly yellow oil solidified on cooling, to a hard crystalline cake. Loss of water during the heating:

Subst., 0.492; loss of weight on heating, 0.018. Calc. for $C_{22}H_{42}O_4$: H_2O , 3.53. Found: 3.65.

The crude product melted at $42-43.5^\circ$. It was purified by dissolving it in ether, and then adding a little more than an equal volume of absolute alcohol. On cooling in ice water it separated in fine, white, asbestos-like needles, which melted sharply at $45-45.5^\circ$ to a clear oil.

Calc. for $C_{22}H_{40}O_3$: C, 78.05; H, 12.20. Found: C, 77.71; H, 12.07.

This anhydride is extremely soluble in ether and practically insoluble in cold alcohol and water.

Hydrolysis of the Above Anhydride and Its Conversion into a Ditetradecylsuccinic Acid Melting at 95° .—This anhydride is quite stable even toward boiling water. When warmed with water it melted, forming a clear layer of oil. Even after boiling for four or five minutes, the oil remained on the surface of the water apparently unchanged. On cooling the oil solidified, forming a crystalline crust which melted at 45° . The water remained perfectly clear, showing that not a trace of hydrolysis had occurred. The anhydride was accordingly boiled for about three-quarters of an hour with 75 cc. of potassium hydroxide (1%). It readily dissolved, forming a milky, or opalescent solution. After filtering and acidifying with dilute hydrochloric acid, a light flocculent precipitate separated. This was dissolved in a small amount of ether, and the solution placed in a freezing mixture of ice and salt. There soon separated a light flocculent precipitate. This substance melted at 95° , forming a slightly turbid oil which became clear at $96-97^\circ$. It decomposed at $145-150^\circ$ with evolution of bubbles.

Calc. for $C_{22}H_{42}O_4$: C, 75.29; H, 12.16. Found: C, 75.10; H, 12.34.

It readily dissolves in warm dilute ammonium hydroxide, and is reprecipitated when acidified with hydrochloric acid. This acid is characterized, in comparison with the acid melting at $135-136^\circ$, by a greater degree of solubility in most of the common organic solvents. It is rather sparingly soluble in cold alcohol, and is more soluble in warm ether than in warm alcohol. It will not separate, however, from an extremely concentrated alcoholic solution. It is difficultly soluble in petroleum ether. It can be crystallized from glacial acetic acid, from which it separates as a light precipitate which, when dry, can be readily reduced to a fine powder. Especially striking is the behavior of the oil obtained by heating the acid a few degrees above its point of decomposition. If the acid is decomposed in a capillary tube, the resulting oil does not solidify on standing for a short time at room temperature. But on sudden cooling, by plunging the capillary into ice water, it solidifies. As soon as it is removed from the ice water it again melts to a clear oil at room temperature. When this

oil, however, is now slightly warmed by merely holding between the fingers, it quickly solidifies and then melts at $43-45^{\circ}$. Owing to the very small amount of substance available, it was impossible to make a closer study of these remarkable changes. They suggest, however, the formation of a low melting, unstable anhydride of the acid melting at 95° , which easily changes into the same anhydride as that obtained by heating the higher melting acid.

The properties of the acid melting at 95° , and its composition as indicated by analysis, show it to be a ditetradecylsuccinic acid isomeric with the acid which melts at $135-136^{\circ}$. The analogy with dimethylsuccinic acid and α, α -dimethyladipic acid, in both of which cases the more soluble acid, and the one having the lower melting point of the two inactive isomeric forms, were resolved into the optically active antipodes,¹ indicates that this ditetradecylsuccinic acid just described is probably the *racemic*, while its isomer melting at $135-136^{\circ}$ is the *meso* modification.

Examination of the Sirupy Residues Obtained by the Action of Silver on Bromo- and Iodopalmitic Acid.—The sirupy residues, obtained by the action of silver on the halogen acids, were united and dissolved in aqueous potassium hydroxide (1%). The solution was just neutralized with dilute hydrochloric acid and a slight excess of barium chloride solution added. A copious precipitate formed. This product after standing *in vacuo* over sulfuric acid for several days had somewhat of a sticky, rubberlike consistency. It was extracted in a Soxhlet extractor with ether for several hours, whereupon a considerable portion of the substance went into solution. (See below for the ether-soluble portion.) The ether-insoluble portion, after drying, consisted of hard lumps which were ground in a mortar, and decomposed with dilute hydrochloric acid by heating on a water bath. An oil separated which on cooling solidified to a hard crust. This was broken up, washed several times with water, dried *in vacuo* over sulfuric acid, and extracted in a Soxhlet apparatus with petroleum ether. A grayish white residue remained undissolved in the capsule.

The petroleum-ether extract on evaporation yielded a white crystalline residue, which after one crystallization from ligroin, and another from alcohol, was identified as palmitic acid. It melted sharply at $62.5-63^{\circ}$.

The grayish white residue which remained undissolved by the petroleum ether, was dissolved in a small amount of alcohol. On standing, a substance separated in the form of light flocculent aggregates, which melted at $90-93^{\circ}$ to a thick, translucent liquid, gradually clearing and becoming a perfectly clear oil at 115° . It decomposed with bubbling at about 150° . Despite all attempts to further purify it, it could not be obtained to melt to a *clear oil* at a definite temperature. It is, however, identical in all other respects with the lower melting ditetradecylsuccinic acid, and

¹ Noves and Kvriakides, *Loc. cit.*; Werner and Basyrin, *Ibid.*

is undoubtedly the same acid, but containing a trace of some impurity which persistently clings to it.

The ether extract, obtained by extraction of the barium salts, yielded on spontaneous evaporation of the ether a straw-colored residue having the consistency of vaseline. This was decomposed by warming in a water bath with dilute hydrochloric acid, and the clear oil which separated, extracted with ether. By spontaneous evaporation of the ether, there was obtained a clear, yellow oil. This oil readily decolorizes bromine water, and is soluble in dilute alkalis, from which it is regenerated when acidified. It showed no tendency to crystallize until after standing for about three months, when a crystalline substance separated. The crystals were spread on a porous plate to remove the adhering oil, and then washed with a little cold alcohol, whereby the substance was obtained nearly white. After two recrystallizations from acetic acid, and another from ether in a freezing mixture, it melted at $86-90^{\circ}$ to a slightly turbid oil which became perfectly clear at 100° and decomposed with bubbling at about 150° . It dissolves easily in warm dilute ammonium hydroxide, and is reprecipitated in a flocculent form when acidified with hydrochloric acid. This substance shows all of the properties of the ditetradecylsuccinic acid which melts at 95° .

The oil from which the above acid was obtained showed strong properties of unsaturation. Unfortunately, the amount available was so small that further investigation of it was impossible.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF ACETYLACETONE-THIOUREA.

By WILLIAM J. HALE AND ARTHUR G. WILLIAMS.

Received January 15, 1915.

The constitution of acetylacetone-urea has been shown by de Haan,¹ and again by one of us,² to accord primarily with the formula advanced by Evans³ and at the same time to exist in a tautomeric imino, or colorless form. The ordinary product was considered quinoid in structure and possessed a decided yellow color. The condensation of thiourea with acetylacetone is described by Evans⁴ as proceeding in exactly analogous manner to the condensation of urea with this diketone and yielding two distinct condensation products. From the properties of these two products it seemed that their exact structures might be open to question. de Haan has shown conclusively that the so-called diurimido-acetylacetone

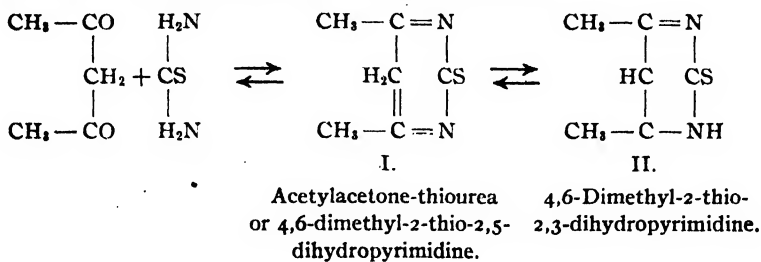
¹ *Rec. trav. chim.*, **27**, 162 (1908).

² *THIS JOURNAL*, **36**, 104 (1914).

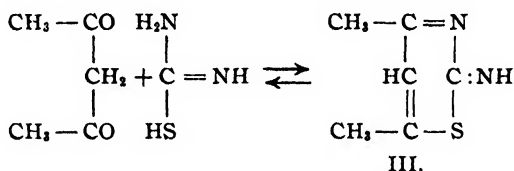
³ *J. prakt. Chem.*, [2] **48**, 489 (1893).

⁴ *Ibid.*, **48**, 503 (1893).

is a pyrimidine at base and not a chain product; in similar manner in a subsequent paper we shall attempt to account for the structure of the so-called dithiourimido-acetylacetone—one of these two condensation products just mentioned. The other product, called by Evans acetylacetone-thiourea, accords with this exact constitution and proceeds from a direct ring condensation between the ketone and thiourea:



The possibility of thiourea condensing in its pseudo form must also be considered. The product would accord with the metathiazine formula (III)



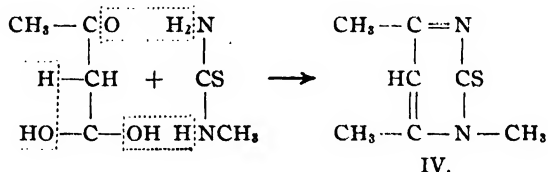
In the former case we might expect a third tautomer bearing a mercaptan group, and in the latter case this identical mercapto compound may easily be derived by the second possible manner of condensation. The possibility of such a result, however, is at once dismissed when it is recalled that acetylacetone-thiourea scarcely blackens moist mercuric oxide or basic lead acetate solution, even by prolonged boiling—a property not in keeping with the presence of a free mercaptan group. This distinct characteristic is almost indicative of Formula III where sulfur is held in the ring. The inference of, however, and the entire basis for such metathiazine structure, is overthrown by the ease with which the *n*-methyl ether of acetylacetone-thiourea gives up its sulfur to these mild desulfurizing agents. We are, therefore, brought to the conclusion that only Formulas I and II can be presented for consideration—structures similar in every respect to the two possible tautomeric formulas for acetylacetone-urea.

The free acetylacetone-thiourea is almost colorless when pure—a point in favor of the tautomeric imino form (II). However, when a thio group is present the absence of marked color cannot be taken as argument against the quinoid structure. In the application of Hinsberg's test for the presence of a secondary amine (or imino) group, only negative results could

be obtained; a result identical with that¹ obtained with acetylacetone-urea, which is known to exist in both keto and imino forms, and consequently due no doubt to the strongly negative thio group. The action of diazomethane upon this acetylacetone-thiourea, both in methyl alcohol and in chloroform solutions, failed to give any appreciable quantity of a methyl ether corresponding to that which was readily and quantitatively prepared when diazomethane acted upon acetylacetone-urea. This result was unexpected and can only be used as an argument against the imino form (II) for the free substance. The compound, therefore, may be regarded as existing primarily in its quinoid structure, namely, that of the 2,5-dihydro derivative (I): a 4,6-dimethyl-2-thio-2,5-dihydropyrimidine. The tendency toward formation of salts is to be looked upon, however, as proceeding from the imino form. The process was found slow and in nowise complete.

The preparation, not only of this *n*-methyl ether but also of the thio ether, was accomplished by condensation of acetylacetone with methyl thiourea, $\text{NH}_2\cdot\text{CS}\cdot\text{NHCH}_3$, and on the other hand with methyl iminothiocarbamate, $\text{NH}_2\cdot\text{C}(\text{SCH}_3)\cdot\text{NH}$, respectively.

The condensation with methyl thiourea proceeded readily in acid solution:

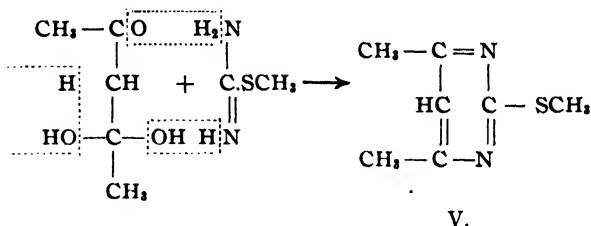


The free substance, melting at 156.5° , is colorless and is easily blackened by warming with mild desulfurizing agents. The resistance of the sulfur in acetylacetone-thiourea to these same agents is therefore no longer apparent when one of the nitrogen atoms carries a substituent. The complete desulfurization of the ether, and replacement of sulfur by oxygen, was accomplished by several hours' boiling with an aqueous solution of chloroacetic acid. The product hereby obtained is naturally identical with that product prepared by the condensation of acetylacetone and methylurea.² The structure (IV) therefore of the ether of acetylacetone-thiourea is established. The desulfurization of acetylacetone-thiourea itself by means of chloroacetic acid was found to give acetylacetone-urea as expected.

Condensation of acetylacetone with methyl iminothiocarbamate, *i. e.*, pseudomethyl-thiourea, proceeded well in alkaline solution:

¹ THIS JOURNAL, 36, 113 (1914).

² *Ibid.*, 36, 114 (1914).



The oil separating out is somewhat difficult to purify, but the free product obtained by distillation *in vacuo* agreed in all respects with the thio ether (m. p. 24°) prepared by Wheeler and Jamieson.¹ We started with the product which Dixon² made by the action of thiourea upon methyl chloro-carbonate. Upon melting this methyl pseudo-thioallophanate, we secured the pseudomethyl-thiourea in the form of its hydrochloride. Wheeler and Jamieson condensed the methyl iodide addition product of thiourea with acetylacetone in the presence of alkali. The structure of their addition product, as investigated by Bernthsen and Klinger³ and by Werner⁴ and others, corresponds with that of a methyl ether of iminothiocarbamic acid in the form of its hydrogen iodide salt and consequently should enter into the condensation in the same manner as the hydrochloride salt employed by us. Furthermore, this thioether or 2-methylmercapto-4,6-dimethylpyrimidine, may best be prepared directly from free acetylacetone-thiourea by methylation with methyl iodide and sodium methylate. No matter by which of these three possible methods the methyl mercapto derivative is prepared, it is slowly transformed into the corresponding keto derivative, with consequent loss of mercaptan, when boiled for several hours with concentrated hydrobromic acid. This keto derivative is again the free acetylacetone-urea melting at 210°. Its production from acetylacetone-thiourea directly or through the intermediate step of a methylmercapto derivative, taken together with its corresponding production in the form of a methyl ether of acetylacetone-urea by the action of chloroacetic acid upon the methyl ether of acetylacetone-thiourea leave no room for doubt upon the constitution of the thiourea condensation product. The free acetylacetone-thiourea therefore may be looked upon as of the quinoid type (I) in equilibrium with a small proportion of the rather inactive imino type (II).

Experimental Part.

Acetylacetone-thiourea (I).—The method employed by Evans was found satisfactory in every respect. Two grams of thiourea were dissolved in 40 cc. of alcohol, 2 g. of acetylacetone then added and during cooling 50

¹ *Am. Chem. J.*, **32**, 356 (1904).

² *J. Chem. Soc.*, **83**, 566 (1903).

³ *Ber.*, **11**, 492 (1878).

⁴ *J. Chem. Soc.*, **57**, 283 (1890).

drops of concentrated sulfuric acid admitted to flask. After a day or two the yellow crystalline mass was filtered off and taken up in water. To this solution freshly precipitated barium carbonate was added to neutral reaction. The clear filtrate from the barium salts was then evaporated to dryness upon steam bath and this mass extracted with absolute alcohol. Upon further evaporation of the clear alcoholic solution to small volume the light yellow colored prisms of acetylacetone-thiourea make their appearance. The pure substance melts at 210° (uncor.). This compound is readily soluble in water or chloroform, from which latter it may be precipitated by ligroin in small colorless crystals; it is fairly soluble in alcohol, crystallizing best from this solvent; it is slightly soluble in benzene, ethylacetate, acetone or ether and insoluble in ligroin. It forms insoluble salts with metal ions of barium, silver and mercury as has been noted by Evans. The preparation of this acetylacetone-thiourea as a hydrochloride, using concentrated hydrochloric acid as a condensing agent, is also described by Evans, but the method was not found as practical as that where sulfuric acid is used.

Complete desulfurization of acetylacetone-thiourea was accomplished by the method of Wheeler and Liddle.¹ Two grams of the substance in solution with 15 cc. of water containing 2 g. of chloroacetic acid were boiled under a reflux condenser for a period of 4 or 5 hours. The mixture was then evaporated upon a steam bath and the residue treated with 90% alcohol. The part remaining undissolved was colorless. This colorless hydrochloride was next dissolved in a little water and the solution almost neutralized with alkali, when it was again evaporated to dryness upon the steam bath. The solid mass was now extracted with benzene to remove the free base. This latter came out of the concentrated benzene solution in colorless prisms melting at 198° and proved to be identical in all respects with the acetylacetone-urea of Evans. The two melted separately, and also when mixed, at this constant point.

Condensation of Acetylacetone with Methyl Thiourea.—One gram methyl thiourea and 1 g. acetylacetone in 10 cc. of alcohol are treated with 20 drops of conc. hydrochloric acid, and the yellow solution allowed to stand. The beautiful yellow prisms of the hydrochloride separate out over night. The hydrochloride was crystallized from alcohol for analysis.

0.2038 g. air-dried salt gave 0.1525 g. AgCl. Calc. for $C_7H_{10}N_2S \cdot HCl$: HCl, 19.13%. Found: HCl, 19.04%.

The free substance—the 3,4,6-trimethyl-2-thio-2,3-dihydro pyrimidine, (IV), may be obtained directly from the hydrochloride by adding alkali to its aqueous solution and extracting this neutral mixture with chloroform. If the original reaction-mixture, before removing the hydrochloride, is allowed to evaporate spontaneously to dryness, and then its aqueous

¹ *Am. Chem. J.*, 40, 549 (1908).

solution neutralized with alkali and extracted with chloroform, practically a quantitative yield of the methyl ether is obtained; any methyl thiourea unacted upon will remain undissolved by the chloroform. This colorless methyl ether is insoluble in ligroin or ether; readily soluble in water, chloroform, acetone or alcohol, crystallizing from concentrated solutions in either; and fairly soluble in ethyl acetate or benzene. It is best purified by crystallization from the latter, giving small needles melting at 156.5° . Prolonged boiling with concentrated hydrochloric is without action upon this product. This therefore verifies its structure as a *n*-methyl ether. By gentle warming with basic lead acetate solution, moist mercuric oxide or ammoniacal silver nitrate, a blackening or sulfide formation is observed.

0.1296 g. subs. gave 22.5 cc. N_2 (26° , 729.1 mm. over H_2O). Calc. for $C_7H_{10}N_2S$: N, 18.19%. Found: 18.36%.

One gram of this ether was dissolved in 15 cc. water containing 1 g. of chloroacetic acid and the mixture boiled in flask under reflux condenser for 3 hours. The contents of the flask were then neutralized with NaOH and extracted with chloroform. The chloroform extract, upon evaporation gave a low melting product which, when recrystallized from benzene, melted at 63° and corresponded in all other characteristics with the methyl ether of acetylacetone-urea (m. p. 63°) described by one of us in a previous paper.

Condensation of Acetylacetone with Pseudomethyl-thiourea.—The preparation of pseudomethyl-thiourea was in exact accord with the method described by Dixon.¹ Methyl chlorocarbonate was allowed to condense with thiourea and the crystalline product heated upon a water bath till the evolution of carbon dioxide had ceased and the hydrochloride of pseudomethyl-thiourea remained as residue. Attempts to condense this pseudomethyl-thiourea with acetylacetone in the presence of acids as condensing agents did not give good results. The tendency for desulfurization is apparent when free acids are present. In the presence of alkali, however, the condensation runs smoothly though here also decomposition into cyanamide has been noted. Five grams acetylacetone were added to a cold aqueous solution of 5 g. pseudomethyl-thiourea hydrochloride in 25 cc. of water containing also 2.5 g. of potassium hydroxide. The clear solution was allowed to stand one day, when an oil was found to have separated. This oil, shaken out with ether, dried over solid potassium hydroxide, and distilled *in vacuo*, gave a small quantity of distillate solidifying when cold to a colorless crystalline substance melting at 24° . This was found identical with the 2-methylmercapto-4,6-dimethylpyrimidine (V) (m. p. 24°) obtained by Wheeler and Jamieson¹ when acetylacetone was condensed in alkaline solution with the methyl iodide addition product by thiourea. Just as the product prepared according to the method of

¹ *Loc. cit.*

Wheeler, so also this product from our preparation was submitted to the action of concentrated hydrobromic acid for 3 to 4 hours under a reflux condenser. Mercaptan was copiously liberated and the contents of flask finally evaporated to dryness upon a steam bath. The residue taken up in water was just neutralized with alkali and again reduced to dryness upon steam bath. From this final residue, by extraction with benzene, a product is obtained which upon crystallization from alcohol melts at 198° and is identical with Evans acetylacetone-urea. The methylmercaptan therefore had been transformed into the corresponding keto derivative.

Methylation of Acetylacetone-Thiourea.—The addition of alkyl haloids to the free sulfur atom of acetylacetone-thiourea, just as with thiourea itself, is naturally to be expected. By the action of sodium methylate upon this addition product, which was made but not analyzed, we should expect to obtain the methyl thio ether or methylmercapto derivative of our pyrimidine. 0.6 g. of sodium was dissolved in 10 cc. methyl alcohol and 3.5 g. of acetylacetone-thiourea added. Into this solution 3.5 g. of methyl iodide (which must not be in excess of calculated quantity) in a few cc. of methyl alcohol were then admitted to the flask and the mixture warmed gently under a reflux condenser (over water bath) till neutral reaction appeared. The methyl alcohol was now removed by evaporation and the residue extracted with ether. The ether removed an excellent yield of the almost pure crystalline 2-methylmercapto-4,6-dimethylpyrimidine melting at 24° . When this latter was treated with concentrated hydrobromic acid, as before described, a quantitative yield of the acetylacetone-urea (198°) was obtained. The methylation, therefore, of acetylacetone-thiourea in its methylmercapto form is readily accomplished through the intermediate step of its alkyl halide addition product.

In attempting to methylate acetylacetone-thiourea by means of diazomethane, as was readily accomplished with acetylacetone-urea,¹ no positive results could be obtained. Methyl alcohol and chloroform also were used as solvents. From both solutions the greater part of acetylacetone-thiourea was recovered. In one or two instances it seemed that traces of both the thio ether and the imino ether were present but confirmatory tests were lacking. We are led therefore to the conclusion that acetylacetone-thiourea functions primarily as a quinoid base. The formation of thio ethers is only possible through the preliminary addition of an alkyl salt and consequently all tests to show the possible tautomerization for existence of mercapto group in this free base must have failed. The imino form then must be considered the normal tautomer and in reactivity placed far below the corresponding imino form of acetylacetone-urea.

ANN ARBOR, MICH.

¹ *Loc. cit.*

ON THE DETERMINATION OF SMALL QUANTITIES
OF HYDROCYANIC ACID.

BY ARNO VIEHÖEGER AND CARL O. JOHNS.

Received January 6, 1915.

In our work on cyanogenetic plants we found it necessary to estimate small quantities of hydrocyanic acid. The various titration methods as well as the silver gravimetric methods had to be excluded because we were working with plant distillates which usually contain reducing compounds. Furthermore, the quantities to be determined were often too small to permit the use of the above methods. We frequently had to deal with less than 0.5 mg. of hydrocyanic acid. Chapman¹ has shown that the picric acid colorimetric method of Waller² is not applicable to plant distillates which usually contain reducing substances other than hydrocyanic acid. This left two colorimetric methods to be examined, namely, the thiocyanate method and the Prussian blue method.

In the thiocyanate method of Francis and Connell³ the hydrocyanic acid is distilled into a solution of potassium hydroxide, yellow ammonium sulfide is added and the solution is evaporated to dryness. The residue is dissolved in water, acidified with hydrochloric acid and the mixture is filtered to remove sulfur, after which the filtrate is further acidified and boiled to cause precipitation of the free sulfur. The process of boiling and filtering is repeated until all of the sulfur has been removed from the filtrate. Ferric chloride is then added to the filtrate and the color of ferric thiocyanate is obtained. After an examination of this method we found that it was not accurate enough for our work. Our two chief objections to this method are as follows:

In boiling an acid solution of a thiocyanate, some free thiocyanic acid is lost because it is volatile, the boiling point of the acid being 85°. This loss was shown by taking two equal quantities of potassium thiocyanate, diluting both portions with water, acidifying with hydrochloric acid and boiling one of them for ten minutes in an Erlenmeyer flask. The boiled solution was then cooled. Both the boiled and unboiled portions were tested by adding equal quantities of ferric chloride. The portion that had been boiled gave less color than the one not boiled. This test was repeated and we found that in every case boiling resulted in a loss of thiocyanic acid.

The second important objection to the thiocyanate method is based on the nature of the reaction between a thiocyanate and ferric chloride, $\text{FeCl}_3 + 3\text{KCNS} \rightleftharpoons \text{Fe}(\text{CNS})_3 + 3\text{KCl}$. The equilibrium of this reaction is so easily disturbed by the addition of ferric chloride, intensifying the color, or the addition of other salts, diminishing this color, that it is

¹ *The Analyst*, 35, 471 (1910); 36, 269 (1911).

² *Proc. Royal Soc., (B)* 82, 574, 1910; *The Analyst*, 35, 406 (1910).

³ *THIS JOURNAL*, 35, 1624 (1913).

difficult to adjust conditions so as to obtain constant results. Changes of temperature also have a marked influence on the density of the color.

In recent years several papers have been published on the formation of Prussian blue from cyanides and the colorimetric estimation of the cyanide by comparison with a standard suspension of Prussian blue. The most careful attempts to arrive at a quantitative method seem to have been made by Berl and Delpy and by Lander and Walden.

Berl and Delpy¹ make the solution to be tested alkaline with potassium hydroxide, add a solution of ferrous sulfate, allow the mixture to stand at room temperature for at least ten minutes, shaking frequently, and finally boil for two to fifteen minutes. The resulting mixture is cooled and then acidified with hydrochloric acid. In the case of very dilute solutions of hydrocyanic acid, Berl and Delpy shake out the acidified solution with ether eight to ten times, and shake out the ether with a small quantity of potassium hydroxide solution, thus obtaining the hydrocyanic acid in a more concentrated form.

The method of Berl and Delpy has been improved by Lander and Walden.² These workers concentrate dilute alkaline solutions of hydrocyanic acid by boiling, the final concentrating being carried out in a test tube almost to dryness. The small quantity of liquid left is then cooled and ferrous sulfate solution added. The mixture is allowed to stand ten minutes, with frequent shaking, then acidified with hydrochloric acid and warmed gently.

Vorländer³ investigated the formation of Prussian blue from cyanides. He adds a solution of ferrous sulfate to the alkaline solution of the cyanide and boils for one to two minutes. He then filters and acidifies the filtrate with hydrochloric acid, after which he adds a cold, freshly prepared, saturated solution of ferrous sulfate. He allows the mixture to stand until the maximum color is obtained.

Knight⁴ adds to the alkaline distillate containing hydrocyanic acid, solid ferrous sulfate, then a solution of ferric chloride and boils for one minute. Hydrochloric acid in excess is then added to the hot solution. The precipitate of Prussian blue is filtered, washed with alcohol, and dissolved in a sufficient quantity of sodium hydroxide solution. This solution is acidified with acetic and hydrochloric acids, ferric chloride is then added and any brown color is removed by adding more hydrochloric acid. The mixture is concentrated to about one-half the original volume and the precipitate of Prussian blue, after filtration, is determined by weighing.

¹ *Ber.*, 43, 1430 (1910).

² *The Analyst*, 36, 266 (1911).

³ *Ber.*, 46, 181 (1913).

⁴ *J. Ind. Eng. Chem.*, 6, 909 (1914).

In a method involving the quantitative estimation of a substance by means of colorimetry, it is obvious that a given quantity of the substance should always produce a given density of color in a given volume of solution. It is also necessary that the shade of color should always be the same. For instance, a blue solution cannot be compared accurately with a blue-green solution. Our aim in this work has been to obtain a constant shade as well as density of color. We have studied the following conditions which influence the formation of Prussian blue and the shade of the suspension.

Influence of Concentration on the Formation of Prussian Blue.

Berl and Delpy found that they obtained less Prussian blue from given quantities of hydrocyanic acid in a dilute than in a concentrated solution. These authors, therefore, concentrated dilute solutions of hydrocyanic acid by shaking out with ether as previously mentioned. They state that in this manner nearly all of the hydrocyanic acid can be obtained. In our attempts to concentrate the hydrocyanic acid by means of ether, we found that we could not obtain nearly quantitative results. These low results are due partly to the loss of hydrocyanic acid which will occur by evaporation of the ether. This evaporation cannot be prevented at room temperature, since the acid solution has to be shaken out eight to ten times with ether. Moreover, the volume of alkali needed to extract the hydrocyanic acid from the ether will be so great that the maximum quantity of Prussian blue can scarcely be expected, as shown below.

Lander and Walden, finding also less precipitate of Prussian blue in dilute than in concentrated solutions of hydrocyanic acid, boiled the alkaline solution down almost to dryness. They state that this could be done without the loss of hydrocyanic acid.

The influence of concentration is indeed a very important factor. We made a series of experiments, using 1 mg. of potassium cyanide in each case and concentrations ranging from less than 1 cc. to 10 cc. In a dilution of 10 cc. less than one-half as much Prussian blue was obtained as when the volume was only 1 cc. We found that the maximum color was obtained only when the volume of solution to be tested was not greater than 1.5 cc., while in greater volumes the density of the color decreased with the increasing volume. Where the quantity of potassium cyanide was more than 1 mg. the volume of the solution to be tested could be somewhat increased without loss.

Hence, working with the methods of Berl and Delpy or Knight, where larger volumes than those mentioned above are used, the maximum quantity of Prussian blue would not be obtained.

To test the method of concentrating used by Lander and Walden, we evaporated 25 cc. of an alkaline solution of a cyanide to 1 cc. in a distilling flask and lost almost one-third of the cyanide. When the final evapora-

tion was performed in a test tube the loss was less but still considerable. Hence, it appears that the method of Lander and Walden also cannot give the maximum quantity of Prussian blue, since these authors evaporate over a free flame. It may be mentioned in this connection that evaporation in an open dish on a steam bath resulted in still greater losses than those mentioned above.

After numerous failures we found that alkaline solutions of hydrocyanic acid can be concentrated without appreciable loss by distilling under diminished pressure, as described below.

Influence of Salts on the Formation and Precipitation of Prussian Blue.

Vorländer states that the presence of salts delays or prevents the formation of Prussian blue. We tried the addition of salts, because in our early experiments we often obtained what seemed to be a colloidal form of Prussian blue. Since salts are known to precipitate colloids we tried the effect of adding sodium chloride and found that a clearer blue color was obtained than without the addition of this salt. We also tried the effect of several other halogen salts. Finally, we found that the presence of potassium fluoride had a remarkable effect on the formation and color of the Prussian blue. On acidifying in the final stage of the test the color appears at once and is very brilliant. The absence of a green shade makes it particularly suitable for comparison with a standard. If the acid is added very gradually the iron hydroxides dissolve and a colorless liquid with a white precipitate is obtained. On the addition of more acid the blue color appears. This is explained by the fact that ferric salts produce a complex salt with potassium fluoride,¹ K_3FeF_6 . When an excess of acid is added this complex salt is decomposed and the ferric ions needed for the formation of Prussian blue are furnished. Contrary to the statement of Vorländer, our experiments show that certain salts, such as sodium chloride and particularly potassium fluoride, hasten the formation of Prussian blue.

Influence of Acids on the Formation of Prussian Blue and on the Color of the Suspension.

Previous workers all seem to have used hydrochloric acid in the final stage of the test for a cyanide to precipitate the Prussian blue. We found that an excess of this acid tends to make the color of the suspension green, owing to the formation of ferric chloride. The mixture of the yellow ferric chloride solution with the Prussian blue produces the green shade. To avoid the formation of the green shade we tried the effect of acids other than hydrochloric acid. We obtained good results with sulfuric and nitric acids in different concentrations. Hence, these acids are recommended instead of hydrochloric acid.

¹ Greef, *Ber.*, 46, 2511 (1913).

Vorländer and Knight both filter off the iron hydroxides from the alkaline solution of sodium ferrocyanide and then acidify *before* adding the iron salt. This procedure may lead to a loss of hydrocyanic acid, since ferrocyanic acid oxidizes rapidly according to the following equation:



Influence of Ferric Iron on the Formation of Prussian Blue and on the Color of the Suspension.

It is to be noticed that Berl and Delpy, Lander and Walden, as well as Vorländer, used only ferrous sulfate for the formation of small quantities of Prussian blue. In the ordinary laboratory test for a cyanide, ferric chloride is also added, which changes the color to a greenish shade and makes accurate colorimetric determinations impossible. The addition of a ferric salt is not necessary, since enough of the ferrous salt is oxidized during the operation to furnish the ferric ions needed. According to our experience it is very important that there should not be a large excess of ferric salts present. Therefore, to prevent the oxidation of too much of the ferrous hydroxide to ferric, we remove most of the air from the solutions of the cyanide by means of a water vacuum pump.

In this connection we may quote Vorländer's statement.¹

"Die Meinung ist verbreitet, dass zum Zustandekommen des Berlinerblaus aus Ferrocyankalium die Gegenwart von Ferro- und Ferrisalz nützlich sei. Ich habe hierfür nicht das geringste Zeichen finden können."

Here one might obtain the misleading impression that Prussian blue is formed in the utter absence of a ferric salt. Vorländer probably means to say that the addition of ferric salt is unnecessary, as enough of the ferrous salt is oxidized by the action of atmospheric oxygen to furnish the ferric ions needed.

Influence of Heat on the Formation of Prussian Blue.

It is interesting to note that other workers apply heat in the test for a cyanide. Sometimes the alkaline mixture is heated, and sometimes heat is applied after adding the acid. Others recommend that the mixture be heated, both before and after the addition of acid. In testing by our method heat is not necessary if potassium fluoride is used. In using sodium chloride instead of potassium fluoride, or in the absence of these salts, gentle heat hastens the formation of Prussian blue.

Description of the Method.

As a result of our various experiments, we recommend the following procedure: Before concentrating the hydrocyanic acid solution, as in the case of a distillate, the portion to be tested should contain a slight excess of free sodium hydroxide. We used 0.02 to 0.1 g. This solution is then concentrated in a round bottom flask of 200 cc. capacity by using

¹ *Ber.*, 46, 188 (1913).

a vacuum pump and condenser. The heat is supplied by immersing the flask in a water bath kept below 70° . To avoid any loss by spattering the flask is fitted to the condenser by means of an adapter such as is used in the Kjeldahl method for the determination of nitrogen. We concentrate until less than 1 cc. of liquid remains in the flask. Two-tenths to one-half cubic centimeter of 3% freshly prepared ferrous sulfate solution and about 0.05 g. of potassium fluoride are then added. The flask is exhausted at once by means of a water vacuum pump. The contents are mixed by rotating the flask. After 5 to 10 min. the flask is detached from the pump and the mixture acidified with 30% nitric acid. The blue color appears at once. Where only traces of hydrocyanic acid are present it is sometimes necessary to warm to about 50° in a water bath before the color appears. The suspension is then diluted to a volume that would give a color density convenient to compare with a suspension of Prussian blue made from a known weight of potassium cyanide. As a standard we used a suspension of Prussian blue made from 1 mg. of potassium cyanide. Such a suspension diluted to 25 cc. gave a color of convenient density. For comparison we used a Duboscq colorimeter.

If the cyanide solution to be tested was sufficiently concentrated so that further evaporation was unnecessary, the test could be made in a test tube. We kept the air out by means of a stopper and rotated the tube only enough to mix the reagents, allowing the mixture to stand 5 to 10 min. before acidifying. Much shaking must be avoided to prevent excessive oxidation of the ferrous hydroxide.

We ascertained the accuracy of our method by diluting 1 cc. of a standard solution of potassium cyanide to 25 cc. and evaporating under diminished pressure to 1 cc. When the residue was tested as described above we obtained the same quantity of Prussian blue as that formed by applying the test to 1 cc. of the undiluted standard solution.

The quantities of reagents mentioned are suitable for 1 to 2 mg. of potassium cyanide. If less than 1 mg. of potassium cyanide is present, the quantities of the reagents should be reduced accordingly. A large excess of reagents must be avoided in order to obtain the maximum density of color. When the analysis is carried out as described the maximum error should not exceed more than 1 part in 20. Thus in a plant giving 20 mg. of potassium cyanide per 100 g. of plant the results might vary by 0.001% if 100 g. of material are used for analysis.

Application as a Qualitative Test.

This method also proved to be a very delicate qualitative test for the presence of a cyanide. Owing to the possibility of obtaining a pure blue color we were able to detect with certainty 0.00002 g. of potassium cyanide, which represents less than 0.00001 g. of hydrocyanic acid.

Application to Microchemical Analysis.

The test for hydrocyanic acid was applied microchemically to sections of cherry bark and bitter almond with marked success. Sections or small parts of the material were treated with the reagents in a test tube according to our method.¹

Conclusions.

1. Dilute alkaline solutions of a cyanide can be concentrated under diminished pressure without appreciable loss of cyanide.

2. The maximum quantity of Prussian blue can be obtained from a cyanide only when the volume of the solution to be tested is sufficiently small, as has been indicated by Berl and Delpy and by Lander and Walden.

3. In the test for a cyanide it is better to acidify with nitric or sulfuric acid than with hydrochloric, since an excess of the latter tends to produce a green color.

4. Any considerable excess of ferric salts should be avoided in testing for a cyanide.

5. Application of heat is not necessary in testing for a cyanide by the method described.

6. The presence of certain salts, particularly potassium fluoride, in the liquid to be tested, has proved to be of great advantage.

7. The method furnishes a very delicate qualitative test for the presence of a cyanide.

8. The method is suitable for the estimation of very small quantities of a cyanide in distillates.

9. The test as described herein can be applied microchemically to sections of cyanogenetic plants.

BUREAU OF CHEMISTRY,
WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY.]

A COMPARATIVE STUDY OF METHODS FOR THE QUANTITATIVE DETERMINATION OF SULFUR IN PEPTONE

BY HARRY W. REDFIELD AND CLARENCE HUCKLE.

Received January 18, 1915.

As a preliminary step to making quantitative determinations of the amount of sulfur in culture media, both before and after inoculation with sewage or water samples, and before and after incubation, a comparative study was made of those methods for the determination of sulfur in organic compounds which a search of the literature showed as having given the

¹ Further work is in progress on the application of this method to microchemical analysis.

best results in the hands of other investigators. Witte peptone was used as the sulfur-containing material and at least three determinations were made in each case, using two-gram portions of sample.

Methods for Total Sulfur.

The following methods for total sulfur were tried:

Liebig Method.¹—A slight modification of this method was also experimented with, using less heat and larger quantities of potassium nitrate in the fusions.

Osborne Method.²

A. O. A. C. Method.³

Liebig-Koch Method.⁴—After two trials of the method as described in the above reference, it was modified as follows:

The solution of the material, after the nitric acid treatment, was introduced into a nickel crucible containing eight grams of potassium hydroxide and about one-half gram of potassium nitrate and then evaporated over an alcohol lamp while a jet of air was allowed to impinge on the surface of the liquid. This resulted in a homogeneous mixture of the material under examination with the hydroxide and nitrate, thus precluding the tendency to burn which the peptone displayed in earlier determinations. Another device, trivial, but nevertheless worthy of note, was used in connection with the transference of the material, which had been treated with nitric acid, to the nickel crucible. A number of particles difficultly soluble in hot water clung tenaciously to the sides of the beaker. Obviously a rubber-tipped rod could not be used to loosen them because of the danger of minute particles of the rubber becoming detached which might contribute appreciable amounts of sulfur. Therefore, a small piece of filter paper on the end of a glass rod was employed for scrubbing. This effectively loosened all particles. The piece of filter paper with any adhering material was introduced into the nickel crucible and was, of course, destroyed during the alkali-nitrate fusion.

It was deemed advisable to ascertain whether any loss of sulfur in volatile form might take place during the treatment with nitric acid in the Liebig-Koch method.

For this purpose, a 250 cc. ether wash bottle was modified by fusing on a small separatory funnel. The lower end of the entry tube was drawn out and bent into a shepherd's crook. To the other tube, which emerged from the stopper of the wash bottle, was fused a piece of glass tubing which was bent so as to nearly reach to the bottom of a Fritz Friedrich's gas

¹ As described in "Organic Analysis," Sherman, 1912 edition, p. 298.

² THIS JOURNAL, 24, 142 (1902).

³ U. S. Dept. of Agr., Bur. Chem., *Bull.* 107, Revised, p. 23.

⁴ *Chem. Zentr.*, 1886, p. 894.

wash bottle, the connection being made by means of a soft-rolled cork stopper. The glass tube which was fused into the stopper of the Fritz Friedrichs wash bottle was connected with a suction pump.

Two grams of peptone were placed in the ether wash bottle, which was mounted on a boiling water bath and connected to the Fritz Friedrichs wash bottle, into which 250 cc. of 12% potassium hydroxide had been introduced. Suction was applied and 20 cc. of nitric acid (sp. gr. 1.4) was introduced through the separatory funnel. The suction was so regulated that about two bubbles of air per second were drawn through the apparatus. Thus, any volatile compounds of sulfur which might be liberated during the process would be drawn into the potassium hydroxide solution and held there.

It required two weeks, running eight to ten hours a day, to completely distil all of the nitric acid from the ether wash bottle into the Fritz Friedrichs wash bottle.

The material in the ether wash bottle was then dissolved in hot water and transferred to a Jena glass beaker, acidified with hydrochloric acid, evaporated to dryness on a water bath, 20 cc. of distilled water added, again evaporated to dryness, heated for 4 hours in an air bath at 110° to dehydrate the silica, dissolved in water, 5 cc. of hydrochloric acid added, filtered, and the sulfur existing as sulfuric acid, precipitated and weighed as barium sulfate.

For comparison, the amount of sulfur existing as sulfuric acid after treatment of peptone with nitric acid in open beakers was determined.

For this purpose, 2 g. portions of peptone were placed in Jena glass beakers, 20 cc. of nitric acid (sp. gr. 1.4) were added to each, and digestion was carried on for two hours on a water bath; each solution was then evaporated to dryness, 20 cc. of distilled water added, again evaporated to dryness, heated for 4 hours in an air bath at 110°, dissolved in water, 5 cc. of hydrochloric acid added, filtered, and the sulfur existing as sulfuric acid precipitated and weighed as barium sulfate.

The close agreement between the results obtained in the closed system and in the open beakers, while not proving that there is no loss of volatile sulfur compounds, does prove that the length of time of the digestion with nitric acid above two hours has no effect, as the nitric acid was in contact with the peptone for two hours in the one case and for two weeks in the other.

To ascertain whether any loss had taken place during the nitric acid treatment in the closed system, the amount of sulfur in the solution contained in the Fritz Friedrichs wash bottle was determined.

For this purpose, the solution—which was calculated to contain 30 g. of potassium nitrate, resulting from the neutralization of the 18.3 g. of nitric acid distilled over from the ether wash bottle plus 14 g. of potassium hydroxide remaining from the 30 g. originally introduced in the form of 250 cc. of 12% potassium hydroxide, together with any potassium sulfide, potassium sulfite or potassium sulfate which might have been formed—was transferred to a large nickel crucible, evaporated to dryness and fused, in order that any sulfide or sulfite might be oxidized to sulfate. The fused mass was dissolved in water, an excess of hydrochloric acid added, evaporated to dryness, 20 cc. of distilled water added, again evaporated to dryness, heated for 4 hours in an air bath to 110° to dehydrate the silica, dissolved in water, 5 cc. of hydrochloric acid added, filtered, and precipitated with barium chloride in the usual manner.

The results showed that there was no formation of volatile sulfur compounds during the nitric acid digestion in the closed system; and since the results in the open beakers were in such close agreement with those obtained in the closed system in the matter of the percentage of sulfur revealed by nitric acid digestion, it is safe to assume that no loss of sulfur as volatile compounds occurs during nitric acid digestion in open beakers.

Petersen Method.¹

Perhydrol Method.—It was thought that very complete and rapid oxidation of the sulfur-containing organic compounds might be obtained by substituting perhydrol for the 3% hydrogen peroxide used in the Petersen method. Without giving the details of the methods employed, suffice it to say that—dissolving the peptone in water and then boiling with perhydrol—dissolving the peptone in alkaline solution and then boiling with perhydrol—digesting the peptone with nitric acid (sp. gr. 1.4) and then boiling with perhydrol, were all tried without success.²

Parr Calorimetric Method, employing for each charge a mixture of 1 g. of peptone, 15 g. of sodium peroxide and 1 g. of potassium chlorate.

Methods for Part of Sulfur Only.

Schultz Method, for loosely bound sulfur, described by Osborne.³

Nitric Acid-Potassium Chlorate Method.—The effect of a saturated solution of potassium chlorate in nitric acid was next tried upon peptone for the reason that it was believed that this reagent would give a measure of the *easily oxidized sulfur* present.

The method consisted in digesting 2 g. of peptone with 20 cc. of a saturated solution of potassium chlorate in nitric acid in a Jena glass beaker on a water bath for two hours, then evaporating to dryness, adding 5 cc. of hydrochloric acid and 20 cc. of water and evaporating to dryness, dehydrating, and determining the sulfur as barium sulfate.

Hydrochloric Acid-Potassium Chlorate Method.—Determinations were made using potassium chlorate and hydrochloric acid as the oxidizing agent.

Sulfur in Untreated Peptone.

The amount of sulfur precipitable as barium sulfate in a solution of peptone which had not been treated in any way was determined.

Results of Methods.

The average results for all of the foregoing methods appear in Table I.

¹ *Z. anal. Chem.*, 42, 406.

² This work was repeated by Miss M. I. Henkel several months later with the same results.

³ *THIS JOURNAL*, 24, 140 (1902).

TABLE I.

| All determinations were made in triplicate. | Uncor. per cent. of S in peptone. | Per cent. moisture in peptone. ¹ | Per cent. S con- tributed by reagents. | Per cent. S in peptone cor. for moisture and for sulfur contr. by reagents. |
|--|---|---|---|--|
| Liebig method (KOH, KNO ₃ fusion)... | 0.9282 | 6.19 | 0.0040 | 0.9902 |
| Liebig method. Less heat and more KNO ₃ | 0.9067 | 6.19 | 0.0048 | 0.9665 |
| Osborne method (Na ₂ O ₂ fusion)..... | 0.8888 | 6.19 | 0.0000 | 0.9479 |
| A. O. A. C. method (Na ₂ O ₂ , Na ₂ CO ₃ fusion)..... | 0.9122 | 6.19 | 0.0056 | 0.9664 |
| Liebig-Koch method (HNO ₃ digestion and KOH, KNO ₃ fusion)..... | 0.9479 | 6.19 | 0.0041 | 1.0061 |
| HNO ₃ digestion in closed system..... | 0.5005 | 6.19 | 0.0012 | 0.5323 |
| HNO ₃ digestion in open beakers..... | 0.4999 | 6.19 | 0.0012 | 0.5318 |
| Distillate from HNO ₃ digestion in closed system..... | 0.0041 | 6.19 | 0.0043 | 0.0000 |
| Petersen method (digestion with H ₂ O ₂ in alkaline solution)..... | 0.2770 | 6.19 | 0.0072 | 0.2876 |
| Perhydrol method (digestion with 30% H ₂ O ₂ in alkaline solution)..... | 0.2927 | 6.19 | 0.0089 | 0.3025 |
| Modified perhydrol method (digestion with HNO ₃ followed by digestion with 30% H ₂ O ₂)..... | 0.5667 | 6.19 | 0.0097 | 0.5938 |
| Parr calorimeter..... | 0.9142 | 6.19 | 0.0009 | 0.9736 |
| Schultz method for loosely bound S.... | 0.3610 | 6.19 | 0.0031 | 0.3813 |
| HNO ₃ , KClO ₃ meth. for easily oxid. S... | 0.4899 | 6.19 | 0.0007 | 0.5194 |
| HCl, KClO ₃ method..... | 0.0723 | 6.19 | 0.0010 | 0.0761 |
| Untreated peptone..... | 0.0004 | 6.19 | 0.0000 | 0.0004 |
| Alc. extr. of peptone, Liebig-Koch meth. | 0.7013 | 12.30 | 0.0041 | 0.7950 |
| Res. insol. in alc., Liebig-Koch meth.... | 0.9974 | 7.71 | 0.0041 | 1.0763 |

Summary.

1. Of the methods tried, the Liebig-Koch method for total sulfur gave the highest and most consistent results.
2. During the preliminary treatment with nitric acid in the Liebig-Koch method no sulfur is lost in volatile form.
3. The length of time beyond two hours during which nitric acid is allowed to act has no influence in the Liebig-Koch method.
4. Of the methods for determining a part only of the sulfur, the Schultz method for loosely bound sulfur, and the digestion with nitric acid and potassium chlorate for easily oxidized sulfur gave the most consistent and most valuable results.

ITHACA, N. Y.

¹ Determined by drying at 70° for 30 hours in vacuum over CaCl₂.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, CORNELL UNIVERSITY.]

QUANTITATIVE DETERMINATIONS OF SULFUR IN THE CULTURE MEDIUM FOR THE DETECTION OF THE BACTERIA PRODUCING HYDROGEN SULFIDE.

BY HARRY W. REDFIELD AND CLARENCE HUCKLE.

Received January 18, 1915.

By the use of the methods which had been found to give the best results in the determination of sulfur in peptone, as presented in the preceding paper, a study was made of the total amount of sulfur broken down by the so-called putrefactive bacteria in an unadjusted culture medium, containing 3% of Witte peptone and 0.75% of potassium chloride after inoculation; of the forms of sulfur most readily used by them, and of the forms in which the sulfur existed after the action of the bacteria, whether as fixed sulfur, or as loosely bound sulfur, or as easily oxidized sulfur, or as a volatile sulfur compound such as hydrogen sulfide.

Sulfur in Insoluble Residue.—Determinations were first made of the total sulfur by the Liebig-Koch method in that part of the peptone which is agglomerated and which appears as an insoluble residue when peptone is boiled with water, in order to ascertain whether this material contained such a large amount of sulfur that its removal by filtration might have an effect upon hydrogen sulfide production.

It was found that so small an amount of sulfur would be removed in this way that peptone solutions may be filtered without detriment to the medium.

Peptone and Sulfur Used Up by Bacteria in Flasks of Different Size.—In order to ascertain the amount of peptone used up by the bacteria and also the amount of sulfur used in flasks of different size, when the simple peptone medium was inoculated with artificial sewage and incubated, 23 flasks of 100 cc. capacity were prepared by introducing into each, 10 cc. of 30% peptone solution and 5 cc. of 10% potassium chloride solution, after which the flasks were plugged, sterilized and capped and then 85 cc. of artificial sewage which had been strained through sterile cloth into a sterile beaker was added to each flask. Also one flask of 2000 cc. capacity was prepared by introducing into it 200 cc. of 30% peptone solution and 100 cc. of 10% potassium chloride solution after which it was plugged, sterilized and capped and 1700 cc. of the same strained artificial sewage added to it as was used in the 100 cc. flasks.

Two thousand cubic centimeters of a mixture of 30% peptone solution, 10% potassium chloride solution, and artificial sewage in the same proportions as was used in both the small and large flasks above mentioned, was prepared and sterilized to serve as a blank. The flasks containing the inoculated culture media were incubated for 48 hours at 38°.

Effect of Potassium Chloride and of Sewage on Sulfur Determinations.—The grams per 100 cc. of total solids, the grams per 100 cc. of total sulfur by the Liebig-Koch method and the grams per 100 cc. of easily oxidized sulfur by the potassium chlorate-nitric acid method, were immediately determined in the blank.

If the presence of potassium chloride and of artificial sewage has no influence on the sulfur determinations, then the grams of total sulfur per 100 cc. and of easily oxidized sulfur per 100 cc. divided by 3 and divided by 1.0110 (the specific gravity of a 3% peptone solution) and multiplied by 100, should be very close to 1.0061 and 0.5194, respectively, as found in the preceding paper.

Such computations actually give 0.9957 and 0.5176 and, therefore, it is proved that the Liebig-Koch method for total sulfur and the potassium chlorate-nitric acid method for easily oxidized sulfur are as accurate for the culture media employed as they are for peptone itself.

Sulfur in Cultures.—The cultures from 20 of the 100 cc. flasks were combined and filtered through a large webbed paper filter and the soluble material all washed through with distilled water; then a hole was punched in the bottom of the filter and the insoluble material was washed with distilled water into a tared beaker. The culture in the 2000 cc. flask was treated in like manner.

The soluble portions of the cultures were then evaporated to dryness to drive off all traces of volatile sulfur compounds, such as hydrogen sulfide; dissolved in hot water and made up to 500 cc., when total solids exclusive of potassium chloride, total sulfur and easily oxidized sulfur were determined in measured portions.

TABLE I.

| | Grams per 100 cc. of total solids exclusive of KCl. | | Grams per 100 cc. of unattacked sulfur. | | Grams per 100 cc. of easily oxidized sulfur. | | Per cent. which easily oxidized sulfur is of unattacked sulfur. | | Per cent. of total solids, exclusive of KCl destroyed. | | Per cent. of total sulfur converted into H ₂ S. | | Per cent. of easily oxidized sulfur converted into H ₂ S. | |
|---|---|---|--|---|--|--|--|--|--|--|--|--|--|--|
| | Grams per 100 cc. of total solids exclusive of KCl. | Grams per 100 cc. of unattacked sulfur. | Grams per 100 cc. of easily oxidized sulfur. | Per cent. which easily oxidized sulfur is of unattacked sulfur. | Per cent. of total solids, exclusive of KCl destroyed. | Per cent. of total sulfur converted into H ₂ S. | Per cent. of easily oxidized sulfur converted into H ₂ S. | Per cent. of total solids, exclusive of KCl destroyed. | Per cent. of total sulfur converted into H ₂ S. | Per cent. of easily oxidized sulfur converted into H ₂ S. | Per cent. of total solids, exclusive of KCl destroyed. | Per cent. of total sulfur converted into H ₂ S. | Per cent. of easily oxidized sulfur converted into H ₂ S. | Per cent. of total solids, exclusive of KCl destroyed. |
| Peptone, KCl blank..... | 3.0000 | 0.0302 | 0.0157 | 51.99 | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 100 cc. flasks. Filtrate after 48 hrs.' incub..... | 2.5885 | 0.0145 | 0.0103 | 71.03 | 13.72 | 51.99 | 34.39 | ... | ... | ... | ... | ... | ... | ... |
| 2000 cc. flasks. Filtrate after 48 hrs.' incub..... | 2.8850 | 0.0180 | 0.0106 | 58.89 | 3.83 | 40.40 | 32.48 | ... | ... | ... | ... | ... | ... | ... |
| 100 cc. flasks. Sediment after 48 hrs.' incub..... | 0.0176 | 0.0001 | .. | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 2000 cc. flasks. Sediment after 48 hrs.' incub..... | 0.0121 | 0.0001 | .. | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 100 cc. flasks. Filtrate and sediment comb..... | 2.6161 | 0.0146 | .. | ... | 13.13 | 51.65 | ... | ... | ... | ... | ... | ... | ... | ... |
| 2000 cc. flasks. Filtrate and sediment comb..... | 2.8971 | 0.0181 | .. | ... | 3.43 | 40.07 | ... | ... | ... | ... | ... | ... | ... | ... |

All results are computed to the basis of 3.0 g. of total solids exclusive of KCl per 100 cc. in the blank, 0.0302 g. being taken as the amount of total sulfur.

The insoluble portions of the cultures were evaporated to dryness on the water bath and then dried in a vacuum desiccator over calcium chloride at 75° and weighed. As the amount of material was so small, no attempt was made to determine the easily oxidized sulfur, all of the material being used in each case for the determination of total sulfur. The results are given in Table I.

It should be noted that the ratio of total solids, exclusive of potassium chloride, to total sulfur, is very nearly the same in the soluble and insoluble portions of both cultures. Most of the insoluble material is probably peptone and, therefore, it is of no advantage to separate the soluble and insoluble parts of the cultures for analysis and consequently such a separation was not attempted in the subsequent work reported in this article.

Effect of Amount of Surface Exposed.—The fact that the total solids, exclusive of potassium chloride, total sulfur and easily oxidized sulfur were all markedly lower in the case of the cultures in the 100 cc. flask than in the case of the culture in the 2000 cc. flask demanded explanation. A possible reason was that in the case of 100 cc. flasks there was a greater amount of surface exposed to a greater amount of air and that, in consequence, the bacteria were more energetic and, therefore, decomposed a larger amount of peptone. This idea is at variance with the belief that the organisms producing hydrogen sulfide are anaerobes. In order to test out the validity of this explanation, two Fernbach culture flasks were prepared by introducing into each 500 cc. from a mixture of 400 cc. of 30% peptone solution, 200 cc. of 10% potassium chloride solution and 3400 cc. of strained artificial sewage; two flasks of 500 cc. capacity were prepared by introducing into each 500 cc. of the same mixture; ten flasks of 100 cc. capacity were prepared by introducing into each 100 cc. of the mixture, while the balance of the mixture was used as a blank.

The blank was immediately sterilized to await analysis, while the inoculated flasks of various size and shape were placed in the 38° incubator. Air was drawn through a wash bottle containing 5 : 1000 mercuric chloride solution to take out any hydrogen sulfide in the air, then through one of the Fernbach flasks. It finally passed through a Fritz Friedrichs wash bottle containing 2.5 g. of cadmium chloride in water solution, in order to catch and hold as cadmium sulfide all of the hydrogen sulfide which might be produced by the bacteria in the culture and swept over by the current of air. The speed of the air current was so regulated that one bubble per second passed through the wash bottles.

By means of a portable gas generator,¹ carbon dioxide gas under constant pressure was generated from calcium carbonate and hydrochloric acid and passed first through a wash bottle containing distilled water, then through the other Fernbach flask and finally through a Fritz Friedrichs

¹ A. W. Browne and M. J. Brown, *THIS JOURNAL*, 29, 859 (1907).

wash bottle containing 2.5 g. of cadmium chloride in water solution, to absorb any hydrogen sulfide, generated by the bacteria in the culture. The carbon dioxide generator was so regulated that one bubble of gas per second passed through the wash bottle.

The Fernbach flasks through which air and carbon dioxide, respectively, were being passed, and the other flasks through which no gas was being passed but which were being allowed to incubate in the usual manner, were all left in the 38° incubator for 48 hours. They were then sterilized by heat. Without filtering off the insoluble material, this having been proved to be unnecessary in the previous set of inoculations, the blank and the various cultures were analyzed for total solids, for total sulfur, for easily oxidized sulfur, for loosely bound sulfur by the Schultz method, and for sulfur as hydrogen sulfide.

For making these determinations, except that of sulfur as hydrogen sulfide, the blank and the various cultures were evaporated separately to small volumes, then each was made up to 250 cc. in a measuring flask and measured portions taken for analysis. For the determination of sulfur as hydrogen sulfide, the contents of the cadmium chloride wash bottles were acidified with strong hydrochloric acid, an excess of *N*/10 iodine added and the excess titrated with *N*/10 sodium thiosulfate. The results are given in Table II.

The amounts of total solids, exclusive of potassium chloride, remaining in the media after incubation proved that the bacterial action was most energetic in the Fernbach through which air was passed; next in the cultures having the greatest surface exposed, *i. e.*, in the 100 cc. flasks; next in the cultures in the 500 cc. flasks; and was least energetic in the Fernbach flask through which carbon dioxide was passed; while the amounts of total sulfur remaining, the difference between which and the total sulfur of the blank is a measure of the volatile sulfur compounds produced by the bacteria, proved that the production of volatile sulfur compounds by the bacteria decreased in the same order. Therefore, the orders for general bacterial activity and for hydrogen sulfide production were identical, and in the case of the flora with which this work was done, at least, the organisms producing hydrogen sulfide in largest amounts were aerobes and not anaerobes and for the maximum production of hydrogen sulfide, broad, low flasks giving the maximum surface of culture exposed to air should be used.

Determination of Hydrogen Sulfide.—The fact that the amounts of sulfur, as hydrogen sulfide, found by the method employed were far from being the differences between the total sulfur of the blank and the total sulfurs of the cultures in which sulfur as hydrogen sulfide was determined, demanded attention, as it indicated that the method which had been employed was faulty and that the cadmium chloride had failed to stop all of the hydrogen sulfide evolved. It was, therefore, decided to try an iodine solution instead of the cadmium chloride solution in the wash bottle.

For this purpose, air was drawn for 48 hours, first through a wash bottle containing lead acetate solution to remove any gaseous sulfur compounds, then through a Fernbach flask, containing 500 cc. of the culture medium, artificial sewage mixture

TABLE II.

| | Results are computed to the basis 3.0 g. of total solids excl. of KCl in 100 cc. in the blank. 0.0302 g. being taken as the amount of total S. | | | | | | | | | | | | | |
|---|---|------------------------------------|---|---------------------------------------|---|---|---|---|--------------------------|---|--|---|---|--|
| | G. per 100 cc. of total solids excl. of KCl. | G. per 100 cc. of unattacked S. | G. per 100 cc. of easily oxidized S. | G. per 100 cc. of loosely bound S. | G. per 100 cc. of S as H ₂ S. | % which easily oxi- dized S is of un- attacked S. | % which loosely bound S is of un- attacked S. | Unattacked S plus S as H ₂ S. | % of S accounted for. | % of total solids, excl. of KCl, de- stroyed. | % of total S con- verted into H ₂ S. | % of easily oxidized S converted into H ₂ S. | % of loosely bound S converted into H ₂ S. | |
| Peptone, KCl blank. | 3.0000 | 0.0302 | 0.0157 | 0.0078 | .. | 51.99 | 25.83 | 0.0302 | 100.00 | .. | .. | .. | .. | |
| Culture in Fernbach 4 hrs.... | 2.6520 | 0.0200 | 0.0090 | 0.0041 | 0.00 | 45.00 | 20.50 | 0.0211 | 69.87 | 11.60 | 33.77 | 42.68 | 47.45 | |
| Cul- res in 100 cc. fl. | 2.7209 | 0.0222 | 0.0105 | 0.0049 | .. | 47.30 | 22.07 | .. | .. | 9.30 | 26.49 | 33.12 | 37.18 | |
| Cul- res in 500 cc. fl. 48 hrs. | 2.7872 | 0.0244 | 0.0110 | 0.0055 | .. | 45.08 | 22.54 | .. | .. | 7.09 | 19.21 | 29.93 | 29.49 | |
| Cul- res in Fernbach CO ₂ pas l | 2.8899 | 0.0249 | 0.0096 | 0.0066 | 0.00 | 38.55 | 26.51 | 0.0261 | 86.42 | 3.67 | 17.55 | 38.85 | 15.38 | |
| 4 hrs | | | | | | | | | | | | | | |

TABLE III.

| | 3.0 g. 00 cc. as the | the ba- KCl ing ta- | il result: are computed i of total solids exclusive in the blank, 0.0302 g. amount of total S. | Absorbent. | G. per 100 cc. of total solids excl. of KCl. | G. per 100 cc. of unattacked S. | G. per 100 cc. of S as non-vol. sul- fide. | G. per 100 cc. of S as H ₂ S. | Unattacked S plus S as H ₂ S. | % of S accounted for. | % of total solids, de- stroyed. | % of total S con- verted into H ₂ S. | % of total S con- verted into non- vol. sulfide. |
|---|----------------------------|---------------------------|---|--------------------------------|--|------------------------------------|--|---|---|--------------------------|------------------------------------|--|--|
| Pep one, KCl blank. | | | | | 3.0000 | 0.0300 | 0.0003 | .. | 0.0300 | 99.34 | ... | ... | .. |
| Cu ure in Fernbach. Air passed 72 hrs. | | | | KOH | 2.4915 | 0.0148 | 0.0003 | 0.0154 | 0.0302 | 100.00 | 16.95 | 51.00 | 0.00 |
| Cu ure in Fernbach. Air passed 72 hrs. | | | | CdCl ₂ | 2.5535 | 0.0154 | 0.0009 | 0.0140 | 0.0294 | 97.35 | 14.88 | 49.01 | 1.99 |
| Cu ure in Fernbach. Air passed 72 hrs. | | | | Na ₂ O ₂ | 2.5118 | 0.0133 | 0.0009 | 0.0144 | 0.0277 | 91.72 | 16.27 | 55.96 | 1.99 |
| Cu ure in Fernbach. Air passed 72 hrs. | | | | PbAc ₂ | 2.4023 | 0.0133 | 0.0010 | 0.0112 | 0.0245 | 81.13 | 19.92 | 55.96 | 2.32 |

already described, in the 38° incubator, then through what had been calculated to be an excess of $N/10$ iodine solution in a Fritz Friedrichs wash bottle and finally through a $N/10$ sodium thiosulfate solution in a wash bottle.

During the period of incubation, the iodine solution was found to fade rapidly, indicating that larger amounts of hydrogen sulfide than had been expected were being produced, and consequently, small measured amounts of normal iodine solution were, from time to time, added to the iodine solution in the wash bottle. After 48 hours of incubation, the iodine solution and the sodium thiosulfate solution were mixed together and the amount of iodine which had been used up, determined by titration.

It was found that an amount of iodine equivalent to the hydrogen sulfide which would be produced if nearly all of the sulfur of the medium were transformed to hydrogen sulfide, had been reduced. As determinations of total sulfur showed that only about 25% of the total sulfur had disappeared from the medium the results were evidently impossible. The explanation which is offered is that volatile, unsaturated organic com-

pounds like indol, $C_8H_7\begin{matrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{CH} \end{matrix}=\text{CH}$ and skatol, $C_8H_7\begin{matrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{C}(\text{CH}_3) \end{matrix}=\text{CH}$,

were liberated from the medium by the action of the bacteria and that these reduced the iodine solution.

The use of iodine solution having been proved to be of no value, it was decided to try solutions of cadmium chloride containing potassium chloride to prevent colloidal suspension of cadmium sulfide, of lead acetate containing potassium nitrate to prevent colloidal suspension of lead sulfide, of sodium peroxide and of potassium hydroxide, determining the total sulfur retained as sulfide by the Liebig-Koch method and not by liberating with hydrochloric acid and titrating with iodine and sodium thiosulfate solutions as had been done when cadmium chloride was before used.

The Fernbach flasks containing the usual mixture of culture medium and artificial sewage and the Fritz Friedrichs wash bottles containing the various solutions were connected in parallel to the same suction. The blank was immediately sterilized to await analysis and the Fernbachs were incubated at 38° for 72 hours (allowed to incubate 72 hours because the end of 48-hour period came on Sunday), air being sucked through the Fernbach flasks and their wash bottles at as uniform a rate as possible.

After 72 hours, each Fernbach was heated to boiling on a water bath for 30 minutes while air was sucked through it and its respective wash bottles. This was to drive out all hydrogen sulfide held in solution in the cultures. The solution from each Fernbach was then made up to 500 cc. (only a few cc. had been lost by evaporation in each case), and total solids, total sulfur and sulfur as nonvolatile sulfides determined in measured portions of these cultures and of the blank. The results are given in Table III.

The determination of sulfur as nonvolatile sulfides was accompanied by placing 300 cc. of each culture in a distilling flask and adding 25 cc. of concentrated hydrochloric acid. A Vigreux tube was attached and the solution was then distilled for 30 minutes under reduced pressure into sodium peroxide solution (5 : 60) contained in a wash bottle, the purpose being to decompose the sulfides and to distil the hydrogen sulfide formed into the sodium peroxide where it would be held as sodium sulfide, and possibly sulfate, in which form the sulfur was determined by the Liebig-Koch method.

The sum of the total sulfur remaining in the medium plus the sulfur found as hydrogen sulfide in the wash bottles proved to be 0.0294 g. per 100 cc. when cadmium chloride was used; 0.0245 when lead acetate was used; 0.0277 when sodium peroxide was used and 0.0302 when potassium hydroxide was used; in a number of determinations 0.0302 g. of total sulfur per 100 cc., on the basis of 3 g. of total solids exclusive of potassium chloride per 100 cc., had been found present in the blanks. The indications were, therefore, that potassium hydroxide stopped and held all of the volatile sulfur compounds evolved, while the other substances failed to do so, although cadmium chloride was almost as efficient.

Determinations of Hydrogen Sulfide with Shorter Incubation.—To eliminate the possibility of analytical errors having crept into this important determination, another exactly similar set of inoculations and sulfur determinations (with the exception that the cultures were incubated 48 hours instead of 72 hours) was made. The results are given in Table IV.

In this second set of determinations the results in all ways confirmed those of the previous work. The sum of the total sulfur remaining in the medium, plus the sulfur found as hydrogen sulfide in the wash bottles, proved to be 0.0304 g. per 100 cc. when cadmium chloride was used; 0.0243 when lead acetate was used; 0.0302 when sodium peroxide was used; and 0.0299 when potassium hydroxide was used: showing that cadmium chloride, sodium peroxide and potassium hydroxide were all efficient reagents to use, while lead acetate was not. In subsequent work, the three reagents named were all employed, although potassium hydroxide is preferable because the precipitate of cadmium sulfide tends to stick to the sides of the wash bottles, from which it must be dissolved by the potassium chlorate-nitric acid reagent with a possibility of sulfur being lost as hydrogen sulfide before it can be oxidized by the reagent, while there is a bad tendency toward spattering in the alkaline fusion when sodium peroxide is present, with possibility of loss. Neither of these difficulties is encountered when potassium hydroxide is used to catch and hold the volatile sulfur compounds.

It was very gratifying to have the sums of the volatile and nonvolatile sulfur compounds in the different cultures approximate so closely to the amount of total sulfur found in the blanks, as it showed that the analytical methods which had been adopted are capable of giving results which are surprisingly accurate when one considers the large number of operations, transferences and filtrations incident to the methods.

Mercaptans.—If mercaptans are formed by the action of the bacteria of sewage, they would pass over into the wash bottles, there to be held as metallic derivatives just as hydrogen sulfide would be held, and would be included under what has been designated sulfur as hydrogen sulfide. The amounts of mercaptans formed, if any, would undoubtedly be very

All results are computed to the basis of 3.0 g. of total solids excl. of KCl per 100 cc. in the blank, 0.0302 g. being taken as the amount of total S.

Absorbent.

Peptone, KCl blank.....
Culture in Fernbach. Air passed 48 hrs.....
Culture in Fernbach. Air passed 48 hrs.....
Culture in Fernbach. Air passed 48 hrs.....
Culture in Fernbach. Air passed 48 hrs.....

| TABLE IV. | | | | | | | | | |
|-------------------------------------|--|---------------------------------|--|--|--|-----------------------|---|---|---|
| | G. per 100 cc. of total solids excl. of KCl. | G. per 100 cc. of unattacked S. | G. per 100 cc. of S as non-vol. sulfide. | G. per 100 cc. of S as H ₂ S. | Unattacked S plus S as H ₂ S. | % of S accounted for. | % of total solids, excl. of KCl, destroyed. | % of total S converted into H ₂ S. | % of total S converted into non-vol. sulfide. |
| Peptone, KCl blank..... | 3.0000 | 0.0301 | 0.0002 | .. | 0.0301 | 99.67 | ... | ... | .. |
| CdCl ₂ | 2.8136 | 0.0210 | 0.0008 | 0.0094 | 0.0304 | 100.66 | 6.21 | 30.46 | 1.65 |
| N ₂ O ₂ | 2.9064 | 0.0222 | 0.0014 | 0.0080 | 0.0302 | 100.00 | 3.12 | 26.49 | 3.64 |
| KOH..... | 2.7296 | 0.0189 | 0.0007 | 0.0110 | 0.0299 | 99.01 | 9.01 | 37.42 | 1.32 |
| PbAc ₂ | 2.8035 | 0.0209 | 0.0013 | 0.0034 | 0.0243 | 80.46 | 6.48 | 30.79 | 3.31 |

All results are computed to the basis of 3.0 g. of total solids excl. of KCl in the 100 cc. blanks.

Peptone, KCl blank.....
Culture in Fernbach. Air passed 48 hrs.....
Part of peptone insol. in alcohol, KCl control.....
Culture in Fernbach. Air passed 48 hrs.....
Culture in Fernbach. Air passed 48 hrs.....

| TABLE V. | | | | | | | | | |
|-------------------------------------|--------|--------|--------|--------|--------|--------|------|-------|------|
| | | | | | | | | | |
| Peptone, KCl blank..... | 3.0000 | 0.0303 | 0.0003 | .. | 0.0303 | 100.33 | .. | ... | .. |
| N ₂ O ₂ | 2.7836 | 0.0242 | 0.0006 | 0.0059 | 0.0301 | 99.67 | 7.21 | 19.87 | 0.99 |
| .. | 3.0000 | 0.0324 | 0.0005 | .. | 0.0324 | 100.00 | .. | ... | .. |
| N ₂ O ₂ | 2.8035 | 0.0299 | 0.0009 | 0.0024 | 0.0323 | 99.69 | 6.48 | 7.72 | 1.23 |
| KOH..... | 2.8986 | 0.0303 | 0.0010 | 0.0009 | 0.0312 | 96.30 | 3.38 | 6.48 | 1.54 |

All results are computed to the basis of 3.0 g. of total solids excl. of KCl in the 100 cc. blanks.

TABLE VI.

Peptone, KCl blank.....
Culture in Fernbach. Air passed 48 hrs.....
Culture in Fernbach. Air passed 48 hrs.....
Part of peptone sol. in alcohol, KCl control.....
Culture in Fernbach. Air passed 48 hrs.....
Culture in Fernbach. Air passed 48 hrs.....

| Peptone, KCl blank..... | 3.0000 | 0.0302 | 0.0002 | .. | 0.0302 | 100.00 | .. | ... | .. |
|-------------------------|--------|--------|--------|--------|--------|--------|------|-------|------|
| KOH..... | 2.8430 | 0.0242 | 0.0006 | 0.0064 | 0.0306 | 101.32 | 5.23 | 19.87 | 0.99 |
| CdCl ₂ | 2.8092 | 0.0224 | 0.0013 | 0.0072 | 0.0296 | 98.01 | 6.36 | 25.83 | 3.31 |
| .. | 3.0000 | 0.0228 | 0.0002 | .. | 0.0228 | 100.00 | .. | ... | .. |
| KOH..... | 2.8825 | 0.0225 | 0.0003 | 0.0003 | 0.0228 | 100.00 | 3.92 | 1.01 | 0.44 |
| CdCl ₂ | 2.9220 | 0.0224 | 0.0003 | 0.0001 | 0.0225 | 98.68 | 2.60 | 1.75 | 0.44 |

small and consequently no attempt was made to separate and determine them.

Sulfur in Alcohol Extract of Peptone and in Residue from Alcohol Extraction.—In order to ascertain whether the bacteria present in artificial sewage produce hydrogen sulfide more energetically or less energetically from those portions of peptone which are soluble in alcohol (containing lipoid sulfur) and insoluble in alcohol (containing protein sulfur) than they do from peptone itself, culture media were made, in one of which the part of peptone insoluble in alcohol was substituted for peptone, and in the other of which the part of peptone soluble in alcohol was substituted for peptone. The portions of peptone soluble and insoluble in alcohol which were employed, were obtained in the course of the work described in the preceding article.

Hydrogen Sulfide Production from the Part of Peptone Insoluble in Alcohol.—Two Fernbach culture flasks were prepared by introducing into each 500 cc. from a mixture of 150 cc. of a 30% solution of the part of peptone insoluble in alcohol, 75 cc. of 10% potassium chloride solution and 1275 cc. of strained artificial sewage. The remaining 500 cc. were immediately sterilized and kept as a control to be analyzed. One of the Fernbachs was attached to a wash bottle containing sodium peroxide solution (15:225) and the other was attached to a wash bottle containing potassium hydroxide solution (40:225) arranged as previously described. One Fernbach flask to act as a check, was prepared by introducing into it 500 cc. from a mixture of 100 cc. of 30% peptone solution, 50 cc. of 10% potassium chloride solution and 850 cc. of strained artificial sewage. The remaining 500 cc. were immediately sterilized and kept as a blank to be analyzed. The Fernbach flask was attached to a wash bottle containing sodium peroxide solution (15:225).

The three Fernbachs were incubated for 48 hours at 38°, air in each case being sucked through a test tube containing the same solution as the respective wash bottle, then through the Fernbach flask, and finally through the wash bottle at as uniform a rate as possible. After 48 hours of incubation, each Fernbach was heated to boiling on a water bath for 30 minutes while air was sucked through it and its respective wash bottle. The solution from each Fernbach was then made up to 500 cc. (only 1 cc. to 2 cc. had been lost by evaporation in each case) and total solids, total sulfur, sulfur as nonvolatile sulfide and sulfur as hydrogen sulfide were determined in measured portions. In the determinations of sulfur as nonvolatile sulfide, the distillates were caught in 12% potassium hydroxide solution. The results of the analysis are given in Table V.

In both of the Fernbachs containing the medium made from the part of peptone insoluble in alcohol, much less hydrogen sulfide was produced than had been produced in media made from peptone itself. That this was not due to a less energetic bacterial flora in the artificial sewage than had been used in previous work, is proved by the fact that in the check Fernbach made up with the regular peptone medium and with the same sewage, the amounts of total solids exclusive of potassium chloride, total sulfur, sulfur as nonvolatile sulfide and sulfur as hydrogen sulfide, computed to the basis of 3 g. of total solids exclusive of potassium chloride per 100 cc. in the blank, were 2.7836, 0.0242, 0.0006 and 0.0059 g. per 100

cc., respectively, more than twice as much hydrogen sulfide having been produced as in either of the cultures containing the part of peptone insoluble in alcohol.

Hydrogen Sulfide Production from Part of Peptone Soluble in Alcohol.

—A set of inoculations was made using a culture medium made from the part of peptone soluble in alcohol.

Two Fernbach culture flasks were prepared by introducing into each 500 cc. from a mixture of 150 cc. of a 30% aqueous solution of the part of peptone soluble in alcohol, 75 cc. of 10% potassium chloride solution and 1275 cc. of strained artificial sewage. The remaining 500 cc. were immediately sterilized and kept as a control to be analyzed. One of the Fernbachs was attached to a wash bottle containing cadmium chloride solution (10:225) and the other was attached to a wash bottle containing potassium hydroxide solution (20:225) arranged as previously described. Two Fernbach culture flasks to act as checks were also prepared by introducing into each 500 cc. from a mixture of 150 cc. of 30% peptone solution, 75 cc. of 10% potassium chloride solution and 1275 cc. of strained artificial sewage. The remaining 500 cc. were immediately sterilized and kept as a blank to be analyzed. One of the check Fernbachs was attached to a wash bottle containing cadmium chloride solution (10:225) and the other was attached to a wash bottle containing potassium hydroxide solution (20:225) arranged as previously described. The four Fernbachs were then treated in the manner described on page 620. The results of analysis are given in Table VI.

In both of the Fernbachs containing the medium made from the part of peptone soluble in alcohol, much less sulfur-containing material was broken down and very much less hydrogen sulfide was produced than had been produced in media made from the part of peptone insoluble in alcohol, which in turn had given smaller amounts than had been found in media made from peptone itself. That this was not due to a less energetic bacterial flora in the artificial sewage than had been present in previous tests is proved by the fact that in the check Fernbach flasks made up with the regular peptone medium and with the same sewage, the amounts of total solids exclusive of potassium chloride, of total sulfur, of sulfur as nonvolatile sulfide and of sulfur as hydrogen sulfide, computed to the basis of 3 g. of total solids exclusive of potassium chloride per 100 cc. in the blank, were, in the cases where cadmium chloride and potassium hydroxide, respectively, had been used in the wash bottles, 2.8092, 0.0224, 0.0013, 0.0072 g. per 100 cc.; and 2.8430, 0.0242, 0.0006, 0.0064 g. per 100 cc.

Hence, it is evident that a medium made with peptone as the sulfur-containing material is a better one to use for the detection of the bacteria producing hydrogen sulfide than are media made with the part of peptone soluble in alcohol or with the part of peptone insoluble in alcohol.

Summary.

1. The percentage of sulfur present in the very small part of peptone which is insoluble in water is practically the same as in peptone itself. This explains why, in testing for bacteria which produce hydrogen sulfide, it makes no difference whether the medium is filtered or not.

2. The Liebig-Koch method for total sulfur and the potassium chlorate-nitric acid method for easily oxidized sulfur are as accurate for culture media made from peptone and potassium chloride as they are for peptone itself.

3. The ratio of total solids, exclusive of potassium chloride, to total sulfur is very nearly the same in the soluble and insoluble portions of cultures which have been inoculated with artificial sewage, containing bacteria which produce hydrogen sulfide, and incubated at 38° for 48 hours, and hence the indications are that the insoluble material is mostly peptone.

4. More material is broken down by the bacteria and more hydrogen sulfide is produced in flasks having much surface of the culture exposed to air than in flasks having comparatively little surface exposed.

5. It is noteworthy that, when sterile air was passed over the cultures, about 50% more total sulfur was converted into hydrogen sulfide than when they were exposed to quiescent air; and about 100% more than when sterile carbon dioxide was passed over them. Therefore, in the case of the flora which was used at least, the organisms were most active and produced the most hydrogen sulfide when supplied most freely with air. This fact would appear to be of great importance in connection with work directed toward the elimination of odors arising from septic tanks for sewage disposal.

6. From 25-30% of the total sulfur was converted into hydrogen sulfide when cultures were incubated 48 hours with sterile air passing over the culture, and from 50-60% when incubated 72 hours.

7. The volumetric iodine method for the determination of hydrogen sulfide is not available in the analysis of the gases given off by bacteria inoculated into the simple peptone medium, presumably because of the interference of volatile unsaturated organic compounds.

8. The use of potassium hydroxide is to be preferred for absorbing the hydrogen sulfide generated.

9. The sum of the sulfur remaining in the cultures after incubation plus the sulfur in gaseous form, which is practically all present as hydrogen sulfide, equals the total sulfur present in the cultures before incubation, when the determinations are made by the methods adopted in this investigation.

10. In media made from the part of peptone soluble in alcohol much less sulfur-containing material was broken down and very much less hydrogen sulfide was produced than was found in the media made from the part of peptone insoluble in alcohol, the ratios being about 3 : 5 and 1 : 6. In both of these media, very much less sulfur-containing material was broken down and very much less hydrogen sulfide was produced than in the simple peptone medium, the ratios being, respectively, about 1 : 2 and 1 : 20 in the soluble part of peptone, and 2 : 3 and 1 : 4 in the insoluble part of peptone.

11. As shown by the percentage of total solids exclusive of potassium chloride destroyed, and by the percentage of total sulfur converted into hydrogen sulfide, a larger percentage of sulfur-containing material than of total peptone was broken down, the ratio being about 3 : 1. The fact that the bodies of the bacteria were included in the total solids exclusive of potassium chloride, would not materially influence the ratio.

12. A larger percentage of easily oxidized sulfur than of total sulfur was converted into hydrogen sulfide by the bacteria, the ratio being about 4 : 3. It is evident that if a synthetic medium is to be prepared for the detection of the bacteria producing hydrogen sulfide, work upon which is herewith promised, that the sulfur should be introduced in an easily oxidized form.

13. A larger percentage of loosely bound sulfur than of total sulfur was converted into hydrogen sulfide by the bacteria, the ratio being about 3 : 2.

14. A very slightly greater percentage of loosely bound sulfur than of easily oxidized sulfur was converted into hydrogen sulfide by the bacteria, the ratio being about 10 : 9. There was about twice as much easily oxidized sulfur as there was loosely bound sulfur, both before and after the bacteria had acted upon the medium.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,
No. 245.]

STUDIES ON AMYLASES. VIII. THE INFLUENCE OF CERTAIN ACIDS AND SALTS UPON THE ACTIVITY OF MALT AMYLASE.

By H. C. SHERMAN AND A. W. THOMAS.

Received January 2, 1915.

The reaction most favorable to the activity of malt amylase has been given as acid, neutral and alkaline, by different investigators, and there are also striking discrepancies in the statements regarding influence of salts. To some extent, though not entirely, the confusion has arisen through lack of (or failure to use) adequate or uniform criteria of neutrality.

Baswitz¹ observed that carbon dioxide increased the diastatic activity of malt extract. Later Mohr² confirmed the observation and found that very small amounts of lactic acid could also be used with beneficial effects.

Kjeldahl³ found that very small additions of sulfuric acid (making the reaction of the medium equivalent to 0.0005 *N*) increased the sacchar-

¹ *Ber.*, 11, 1443 (1878); 12, 1827 (1879).

² *Ibid.*, 35, 1024 (1903).

³ *Dingler's Polytech. Jour.*, 235, 379, 452 (1880).

ogenic¹ activity of malt extract, while slightly larger amounts were deleterious.

Detmers,² studying the amylolytic¹ action of malt extract, found slightly greater action on passing a current of carbon dioxide through the solution, or on adding small amounts of citric, phosphoric or hydrochloric acid.

Chittenden and Cummins,³ studying the action of malt extract upon a paste made from carefully washed potato starch, found the optimum activity in a neutral solution containing a small amount of peptone.

Duggan⁴ also reported neutrality as the optimum condition for the action of malt amylase, and in a second paper⁵ recommended the observation of optimum diastatic activity as a method of determining absolute neutrality—a suggestion which was later elaborated in the light of the ionization theory by Wood.⁶

Lintner⁷ likewise specified neutrality as the optimum reaction, while Reychler⁸ recommended the addition of potassium acid phosphate and Effront⁹ reported activation of the enzyme by hydrochloric, hydrofluoric, sulfuric, and phosphoric acids as well as by acid phosphate. Effront further pointed out that the effect of adding free acid is largely dependent upon the purity of the starch and water employed. He was probably the first to realize the great importance of purity of materials in studying enzyme action. Petit¹⁰ also found slight acidity favorable and reported hydrochloric and lactic acids to show optimum activation at those concentrations which best favor the coagulation that occurs on heating a water solution of the enzyme.

Ford,¹¹ on the other hand, insists that malt amylase exerts its optimum activity in strictly neutral solution. He attributes the favorable effects, sometimes resulting from the addition of acids or acid salts, to neutralization of alkaline impurities in the starch or the malt extract used.

Schneidewind, Meyer and Münter¹² find acetic and citric acids favorable at a concentration of 0.001% but injurious at 0.01%. They also report

¹ These terms are used in preference to "saccharifying" and "liquefying" as explained in a previous paper.

² *Z. physiol. Chem.*, 7, 1 (1882).

³ *Studies Yale Laboratory Physiol. Chem.*, 1884-5, p. 36.

⁴ *Am. Chem. J.*, 7, 306 (1885-6).

⁵ *Ibid.*, 8, 211 (1886).

⁶ *Ibid.*, 15, 663 (1893).

⁷ *J. prakt. Chem.*, [2] 36, 481 (1888).

⁸ *Bull. soc. chim.*, [3] 1, 286 (1889).

⁹ *Compt. rend.*, 115, 1324 (1892); *Bull. soc. chim.*, [3] 9, 151 (1893).

¹⁰ *Compt. rend.*, 138, 1231 (1904).

¹¹ *J. Soc. Chem. Ind.*, 23, 414, 477 (1904); see also Ford and Guthrie, *J. Chem. Soc.*, 89, 76 (1906).

¹² *Landwirt Jahrbücher*, 35, 911 (1906).

favorable effects from very small additions of acid phosphate and of alum.

Maquenne and Roux¹ report that the maximum initial activity is obtained in solutions neutral to methyl orange, but that a solution alkaline to this indicator shows the optimum total digestion of starch into maltose and dextrin.

Fernbach and Wolff² find optimum amyloclastic and saccharogenic activities in solutions neutral to methyl orange. Addition of secondary sodium phosphate to such solutions depressed the activity; primary sodium phosphate showed either no effect or a slight activation, the latter attributed by these authors to a failure to secure complete neutrality in the control solution.

Windisch and Derz³ found free sulfuric acid always harmful even in minute amounts, while primary potassium phosphate increased the activity of the amylase.

Heyl⁴ finds that primary potassium phosphate exerts both an activating and a conserving influence upon the enzyme, while neutral phosphate mixture depressed the activity of a freshly prepared malt extract, but increased that of an old extract. He concludes, however, that the activating effect of the phosphate is influenced by the proteins present in the malt extracts with which he worked.

Van Laer,⁵ working at 25°, found that acid phosphate and small additions of phosphoric, acetic, and tartaric acids increased the saccharogenic activity of malt extract without apparent effect upon the amyloclastic action, while in parallel experiments with a commercial amylase preparation the addition of acid seemed always to retard the diastatic action, possibly due to a difference of reaction between the commercial preparation and the malt extract.

In view of the above discrepancies and the fact that experiments to test the influence of salts have usually been subject to uncertainty regarding the reaction of the medium, it seems unnecessary to review the earlier results obtained with salts at this time. Even the extended study by Hawkins⁶ which demonstrated an activation of amyloclastic power by sodium and potassium chlorides is difficult to interpret in other respects because of the lack of neutrality in the digestion mixtures.

Experimental.

In view of the importance of an adequate knowledge of the influence of acids and salts on the activity of the enzyme and especially the definite determinations of the optimum hydrogen ion concentration, the following

¹ *Compt. rend.*, 142, 1059 (1906).

² *Ibid.*, 142, 1216; 145, 261 (1906-7).

³ *Woch. Brau.*, 30, 533; *Chem. Abs.*, 8, 268.

⁴ *J. prakt. Chem.*, [2] 86, 433 (1912).

⁵ *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 14, 203 (1912).

⁶ *Botan. Gazz.*, 55, 265 (1913).

series of experiments covering several acids and salts have been carried on in this laboratory during the past two years. The general plan has been to study one acid at a time, making a systematic series of quantitative determinations of diastatic power with increasing amounts of added acid until the optimum acidity is plainly exceeded and a distinct deleterious effect of the acid is observed, repeating the experiments in the region of the optimum with smaller increments of acid if necessary, in order to establish the optimum point with sufficient precision. The solution showing the optimum acidity was then exactly duplicated (except that no enzyme was added) and its hydrogen ion concentration determined by the electro-metric method.

Since previous workers have employed almost exclusively malt extracts which necessarily contained relatively large and variable amounts of salts and proteins, their results, even if concordant, would not have been conclusive. In the present experiments purified enzyme preparations were used which, while varying considerably in activity and in no case absolutely pure, were much purer and more active than any material available to previous investigators of the influence of acids and salts.

Materials.

Amylase.—The amylase preparations used were made in this laboratory by Miss M. D. Schlesinger as described elsewhere.¹ Before performing an experiment, an accurately weighed portion of the dry preparation would be dissolved in pure water and kept in an icebox at 7° to 8° until used.

Substrate.—The substrate used was soluble starch prepared from potato starch by the Lintner² method of treatment with dilute hydrochloric acid. Four samples of this starch were used, one as purchased and three after further purification. Their properties are as follows:

| | Moisture. % | Reduction. Mg. Cu ₂ O per 2 g. dry starch. | Acidity. Cc. of 0.01 <i>N</i> acid per 2 g. dry starch. |
|----------------|----------------|---|---|
| Starch 1..... | 6.25 | 32.4 | 0.85 |
| Starch 2a..... | 11.28 | 27.3 | 1.00 |
| Starch 2b..... | 3.00 | 32.0 | 1.00 |
| Starch 6..... | 9.50 | 34.5 | 1.76 |

The "reduction" is the amount of cuprous oxide reduced by the starch when 100 cc. of a 2% solution are mixed with 50 cc. of Fehling solution and heated in a bath of boiling water for 15 min.

The acidity of the starch is determined by titration of a solution with 0.01 *N* sodium hydroxide, using rosolic acid as indicator.

Starch 1 was a commercial product. Starches 2a and 2b were prepared by repeatedly washing Starch 1 with distilled water. Starch 6 was also purified from a commercial preparation.

¹ THIS JOURNAL, 35, 1617-22 (1913).

² *J. prakt. Chem.*, [2] 34, 378 (1886).

Water.—Ordinary distilled water was twice redistilled: first from alkaline permanganate solution into a reservoir whence it siphoned into a second flask from which it was distilled again. Phosphoric acid was added to this portion in order to hold any ammonia that might have come from the first distillation. Block tin condensers were used and the final distillate was caught in "Nonsol" bottles, contact with the air being avoided as far as possible.

Activating Agents.—These were carefully purified before trying their effect on the action of the amylase. The salts of the best obtainable grade were recrystallized three times, twice from distilled water and finally from triple-distilled water. The inorganic acids were of the purest "analyzed" reagent quality and were used directly as obtained from the manufacturers, it being deemed impracticable to purify them further. The organic acids were redistilled.

Apparatus.

Thermostat.—The digestions of starch by the amylase were carried out in a bath of ten gallons' capacity. The water in this thermostat was heated to, and kept at 40° by means of three 32 candle power carbon filament lamps, one of which burned continuously while the other two were in series with a relay and a large bulb of mercury containing a nickle contact wire in its narrow neck which served as the temperature control. This temperature regulator was very sensitive, keeping the bath within 0.02° above or below 40° . The water in the bath was stirred constantly and vigorously to ensure an even temperature throughout.

Glassware.—All glassware used to contain the starch solutions and digesting mixtures was kept filled with water when not in use, to avoid weathering and consequent introduction of alkali in the enzyme solutions, the danger of which has already been pointed out by Ford.¹ Before using the glassware each piece was carefully rinsed several times with tap water, then with distilled water and finally with triple-distilled water. The flasks or cylinders were then inverted to drain for a few minutes before using.

Hydrogen-ion Apparatus.—For the measurement of hydrogen ion the gas chain method was used in essentially the same manner as described by L. Michaelis.² A standardized Weston cell was used as the standard source of potential and a tenth normal calomel electrode was used in the hydrogen cell. A galvanometer was used instead of the electrometer described by Michaelis. For the hydrogen electrode, No. 14 gauge platinized platinum wire fused in glass tubing filled with a mercury connection was adjusted in the glass cell containing the solution, the hydroger

¹ *J. Soc. Chem. Ind.*, **23**, 414 (1904).

² Abderhalden's *Handbuch der Biochemischen Arbeitsmethoden*, Vol. V, Part 1, pp 500-524.

ion concentration of which was to be tested. This cell differed from Michaelis' in that a stream of hydrogen (washed by saturated mercuric chloride, strong potassium permanganate solution, strong alkaline pyrogallol, and passed through a tube of cotton to remove spray) was passed through it. Michaelis uses still hydrogen.

After finding the potential given by an unknown solution the hydrogen-ion concentration was found by referring to the chart plotted by S. P. L. Sørensen.¹ If this chart is not available the concentration can be calculated by means of the formula

$$\log H = -\frac{E - 0.3377}{0.0001983 T}$$

where H = concentration of hydrogen ion which we are seeking.

E = difference of potential in volts between the 0.1 N calomel electrode and the hydrogen electrode used.

T = absolute temperature.

The figure 0.3377 is the potential difference of the 0.1 N calomel electrode over the normal hydrogen electrode as determined by Sørensen at 18°.

Method of Determining Saccharogenic Power.

To determine the saccharogenic power an amount of soluble starch sufficient to make 600 cc. of 2% solution was weighed out and transferred to a beaker. Enough sodium hydroxide was added to neutralize the acidity of the starch and the mixture stirred to a paste with about 25 cc. of pure water. This paste was then poured into a 1 l. Erlenmeyer flask containing 300 cc. of boiling pure water, and the contents were boiled for two or three minutes to ensure complete solution of the starch. The flask was then partially cooled and the contents were adjusted to a volume of 420 cc. Seventy cc. were then poured into each of six 100 cc. graduated cylinders. The reagents whose effect on the saccharogenic power were to be determined were then added to the cylinders and the volume of solution in each cylinder was adjusted to the 100 cc. mark with pure water and the cylinders were then placed in the thermostat.

While the cylinders were resting in the water bath, the portions of enzyme solution were carefully measured into six 200 cc. Erlenmeyer flasks by means of a 1 cc. pipet which is accurately standardized and graduated to 0.01 cc. These small Erlenmeyer flasks were then placed in a brass rack and the contents of the cylinders were poured into their respective flasks at intervals of 10 sec. and the rack of flasks with their digestion mixtures placed at once in the water bath. At the expiration of 30 min., 50 cc. portions of mixed Fehling solution were poured quickly into each flask at 10 sec. intervals, corresponding with the addition of

¹ *Comptes-Rendus des Travaux du Laboratoire de Carlsberg*, Vol. 8, 1re Livraison, 1909; also *Biochem. Z.*, 21, 131; 22, 352 (1909).

the starch solution to each flask, so that each mixture had digested for exactly 30 min.

The rack was then placed in boiling water for 15 min., after which the contents of the flasks were filtered through Gooch crucibles with suction. The precipitated cuprous oxide was carefully washed with hot water, followed by alcohol and finally ether. The crucibles were dried in an oven and weighed. After the weight of cuprous oxide, due to the reducing power of starch, is deducted from the total, the saccharogenic power is calculated from the scale of Sherman, Kendall and Clark.¹ Blank experiments showed that the acids and salts studied were all without effect upon Fehling solution.

Data of Typical Experiments.

In order to present the results of the experiments as concisely and clearly as possible, no attempt will be made to record every quantitative

TABLE I.—EFFECT OF ACIDS ON SACCHAROGENIC ACTIVITY.

| Acid added. ¹ | Normal concent. of acid. | Reduction in mg. of Cu ₂ O. | Power. | Acid added. ¹ | Normal concent. of acid. | Reduction in mg. of Cu ₂ O. | Power. |
|---|--------------------------------|--|--------|---|--------------------------------|--|--------|
| 1.—Acetic acid. (0.2 mg. Malt Amylase 46B; 100 cc. 2% Starch 2a in each case.) | | | | 3.—Phosphoric acid. (0.2 mg. Malt Amylase 46B; 100 cc. 2% Starch 2a in each case.) | | | |
| None | Neutral | 166.8 | 266 | None | Neutral | 181.7 | 291 |
| 1.0 cc. 0.02 N | 0.0002 | 284.8 | 472 | 0.1 cc. 0.1 N | 0.0001 | 205.7 | 332 |
| 2.0 | 0.0004 | 283.5 | 470 | 0.2 | 0.0002 | 214.7 | 348 |
| 3.0 | 0.0006 | 299.8 | 503 | 0.5 | 0.0005 | 286.1 | 474 |
| 5.0 | 0.001 | 294.4 | 490 | 1.0 | 0.001 | 228.2 | 371 |
| 10.0 | 0.002 | 273.3 | 452 | 2.0 | 0.002 | 67.0 | 103 |
| 20.0 | 0.004 | 237.8 | 388 | 4.—Phosphoric acid, second series. (0.07 mg. Malt Amylase 118; 100 cc. 2% Starch 6 in each case.) | | | |
| 30.0 | 0.006 | 201.4 | 322 | None | Neutral | 65.2 | 271 |
| 2.—Propionic acid. (0.2 mg. Malt Amylase 46B; 100 cc. 2% Starch 2a in each case.) | | | | 1.0 cc. 0.01 N | 0.0001 | 65.1 | 271 |
| None | Neutral | 171.3 | 272 | 3.0 | 0.0003 | 114.7 | 514 |
| 0.1 cc. 0.1 N | 0.0001 | 210.3 | 339 | 4.0 | 0.0004 | 168.0 | 763 |
| 0.2 | 0.0002 | 268.6 | 443 | 5.0 | 0.0005 | 196.1 | 899 |
| 0.3 | 0.0003 | 279.3 | 463 | 6.0 | 0.0006 | 170.9 | 777 |
| 0.4 | 0.0004 | 276.3 | 461 | 5.—Phosphoric acid, third series. (0.07 mg. Malt Amylase 111A; 100 cc. 2% Starch 6 in each case.) | | | |
| 0.5 | 0.0005 | 282.9 | 468 | None | Neutral | 57.0 | 250 |
| 1.0 | 0.001 | 297.2 | 495 | 4.6 cc. 0.01 N | 0.00046 | 140.4 | 633 |
| 2.0 | 0.002 | 262.0 | 431 | 4.8 | 0.00048 | 138.6 | 627 |
| 3.0 | 0.003 | 250.8 | 411 | 5.0 | 0.0005 | 147.7 | 669 |
| 5.0 | 0.005 | 218.0 | 336 | 5.2 | 0.00052 | 148.1 | 669 |
| 10.0 | 0.01 | 138.9 | 220 | 5.4 | 0.00054 | 145.2 | 655 |
| 20.0 | 0.02 | 52.1 | 80 | | | | |
| 30.0 | 0.03 | 42.1 | 64 | | | | |

¹ THIS JOURNAL, 32, 1082 (1910).

² As explained above, under "Method of Determining Saccharogenic Power," the added acid is contained within the final volume of 100 cc., the volume and the concentration of starch of the completed digestion mixture being the same in all cases.

TABLE I.—EFFECT OF ACIDS ON SACCHAROGENIC ACTIVITY—(Continued).

| Acid added, ¹ | Normal concent. of acid. | Reduction in mg. of Cu ₂ O. | Power. | Acid added, ¹ | Normal concent. of acid. | Reduction in mg. of Cu ₂ O. | Power. |
|---|--------------------------------|--|--------|---|--------------------------------|--|--------|
| 6.—Hydrochloric acid. (0.2 mg. Malt Amylase 43B; 100 cc. 2% Starch in each case.) | | | | 8.—Nitric acid, second series. (0.07 mg. Malt Amylase 118; 100 cc. 2% Starch in each case.) | | | |
| None | Neutral | 134.6 | 213 | None | Neutral | 61.2 | 267 |
| 0.5 cc. 0.01 N | 0.00005 | 148.0 | 234 | 0.5 cc. 0.01 N | 0.00005 | 70.4 | 309 |
| 1.0 | 0.0001 | 171.8 | 274 | 1.0 | 0.0001 | 112.7 | 507 |
| 1.5 | 0.00015 | 214.1 | 346 | 1.5 | 0.00015 | 176.9 | 807 |
| 2.0 | 0.0002 | 224.8 | 366 | 2.0 | 0.0002 | 183.8 | 841 |
| 2.5 | 0.00025 | 208.7 | 337 | 2.5 | 0.00025 | 163.1 | 740 |
| 3.0 | 0.0003 | 176.9 | 282 | 9.—Sulfuric acid. (0.2 mg. Malt Amylase 43B; 100 cc. 2% Starch in each case.) | | | |
| 5.0 | 0.0005 | 74.5 | 117 | None | Neutral | 126.8 | 200 |
| 7.0 | 0.0007 | 36.1 | 55 | 0.5 cc. 0.01 N | 0.00005 | 137.9 | 218 |
| 10.0 | 0.001 | 18.3 | 27 | 1.0 | 0.0001 | 172.6 | 271 |
| 15.0 | 0.0015 | 10.5 | 15 | 2.0 | 0.0002 | 212.0 | 342 |
| 7.—Nitric acid. (0.2 mg. Malt Amylase 46B; 100 cc. 2% Starch in each case.) | | | | 2.5 | 0.00025 | 198.4 | 318 |
| None | Neutral | 162.4 | 258 | 10.—Sulfuric acid, second series. (0.2 mg. Malt Amylase 46B; 100 cc. 2% Starch in each case.) | | | |
| 0.5 cc. 0.01 N | 0.00005 | 201.9 | 325 | None | Neutral | 158.0 | 250 |
| 1.0 | 0.0001 | 255.1 | 418 | 2.0 cc. 0.01 N | 0.0002 | 276.7 | 458 |
| 1.5 | 0.00015 | 290.2 | 482 | 3.0 | 0.0003 | 243.0 | 397 |
| 2.0 | 0.0002 | 292.1 | 485 | 5.0 | 0.0005 | 122.1 | 192 |
| 2.5 | 0.00025 | 275.3 | 454 | 10.0 | 0.001 | 14.1 | 4 |
| 3.0 | 0.0003 | 259.8 | 427 | 15.0 | 0.0015 | 5.1 | 1 |
| 5.0 | 0.0005 | 100.8 | 156 | | | | |
| 10.0 | 0.001 | 21.6 | 33 | | | | |
| 15.0 | 0.0015 | 12.8 | 18 | | | | |

determination, nor to give the data in the order in which they were determined. The object is rather to give the data of the principal experiments in sufficient detail to show the nature of the evidence and in such order as to simplify the discussion.

The data showing influence of acids upon saccharogenic activity are tabulated first.

The optimum solution in the case of acetic, is that one containing 3.0 cc. of 0.02 N acetic acid per 100 cc. of 2% starch solution, which in terms of total concentration of acetic acid is 0.0006 N. Measurement of hydrogen ion concentration in such a solution of acetic acid and soluble starch gave the Sørensen exponent $p_H^+ = 4.2$.

The optimum concentration of propionic acid is 0.001 N. The determination of hydrogen ion in a propionic acid starch solution of this concentration showed $p_H^+ = 4.4$.

¹ As explained above, under "Method of Determining Saccharogenic Power," the added acid is contained within the final volume of 100 cc., the volume and the concentration of starch of the completed digestion mixture being the same in all cases.

In the experiments with acetic and propionic acids recorded in 1 and 2 of Table I the enzyme 46B and the Starch 2a were used throughout. Of the experiments with phosphoric acid which follow, the first series (3) was made with the same enzyme and starch while in the second series (4) both the enzyme and the starch were different, and in the third series (5) still a different enzyme preparation was used, but the starch was the same as in the second series. The purer enzyme preparation gave a lower initial and a higher optimum power but the optimum concentration of acid was the same in the three cases.

In the case of phosphoric acid it will be noted that the optimum activity is found in a solution containing this acid in the concentration of 0.0005 *N*. Measurement of hydrogen ion in this solution showed $p_H^+ = 4.6$.

Inasmuch as the activity was hardly appreciably diminished at a phosphoric acid concentration of 0.00054 *N*, the hydrogen-ion concentration was also measured at that point and found to be $p_H^+ = 4.5$.

Passing now to the experiments with strong acids, it will be seen from the table that hydrochloric acid was tested with the same starch as was used with acetic, propionic and the first series with phosphoric and with a very similar enzyme preparation. The first series with nitric employs the same enzyme and starch as the acetic, propionic and (first) phosphoric; the second series with nitric corresponds exactly in starch and enzyme used, with the second series of experiments on phosphoric. The first series with sulfuric corresponds to the experiments with hydrochloric and the second series with sulfuric to the first with nitric. It is therefore believed that the results obtained with the six different acids are fairly comparable with each other and at the same time adequately safe-guarded against any constant error such as might have been possible had all work been done with one sample of enzyme or of starch.

In Series 6, Table I, the optimum concentration of hydrochloric acid was 0.0002 *N*. The soluble starch solution to which hydrochloric acid had been added to this concentration showed $p_H^+ = 4.2$.

With amounts of acid above the optimum the depression of the power is naturally much greater than for corresponding excesses of the weaker acids.

For nitric acid the optimum point is again found in the 0.0002 *N* concentration of acid, and the activity rapidly falls off in the solutions having a greater concentration of acid. Measurement of hydrogen ion in the optimum solution showed $p_H^+ = 4.4$.

As in the case of hydrochloric acid, the optimum activity with sulfuric acid is obtained in solution having a concentration equal to 0.0002 *N*. Measurement of hydrogen ion in this optimum solution showed $p_H^+ = 4.3$ to 4.4.

Closely connected with the problem of the influence of the acids is that of their neutral salts. Sodium and potassium chlorides, nitrates, and

sulfates have therefore been studied, as well as the primary phosphates which, being both salts and acids, will be considered later. In addition to what has been said above regarding the findings of earlier workers it should be stated that Osborne, in 1895, pointed out¹ that the addition of a small amount of sodium chloride assisted his purified malt amylase preparation to exert its true diastatic power.

In our experiments it has been observed that so long as commercial soluble starch, even of high grade (Starch 1) was used as substrate, the small additions of the salts above mentioned have very little effect, but when the more highly purified soluble starch was used the effect was considerable as will be seen from the tables which follow.

Limitations of solubility and a tendency to salting out of the starch when treated with the Fehling solution precluded experiments at higher concentrations than are shown in the tables.

TABLE II.—EFFECT OF SALTS ON SACCHAROGENIC ACTIVITY.

| Amount of salt added. ² | Molar concent. of salt. | Reduction in mg. of Cu ₂ O. | Power. | Amount of salt added. ² | Molar concent. of salt. | Reduction in mg. of Cu ₂ O. | Power. |
|--|-------------------------|--|--------|--|-------------------------|--|--------|
| 11.—Sodium chloride, first series. (0.07 mg. Malt Amylase 111A; 100 cc. neutral 2% Starch 6 in each case.) | | | | 14.—Potassium chloride, second series. (0.07 mg. Malt Amylase 111A; 100 cc. neutral 2% Starch 6 in each case.) | | | |
| None | 0.00 | 48.7 | 214 | None | 0.00 | 48.7 | 214 |
| 0.4 cc. 4 M | 0.16 | 121.6 | 547 | 4.0 cc. 4 M | 0.16 | 122.6 | 551 |
| 0.5 | 0.2 | 129.3 | 580 | 6.0 | 0.24 | 134.7 | 608 |
| 0.6 | 0.24 | 126.1 | 565 | 10.0 | 0.4 | 138.3 | 622 |
| 0.7 | 0.28 | 136.4 | 614 | 15.0 | 0.6 | 131.8 | 594 |
| 0.8 | 0.32 | 139.6 | 631 | 20.0 | 0.8 | 117.0 | 523 |
| 12.—Sodium chloride, second series. (0.07 mg. Malt Amylase 118; 100 cc. neutral 2% Starch 6 in each case.) | | | | 15.—Sodium nitrate. (0.07 mg. Malt Amylase 118; 100 cc. neutral 2% Starch 6 in each case.) | | | |
| None | 0.00 | 63.7 | 281 | None | 0.00 | 62.2 | 272 |
| 1.0 cc. 4 M | 0.04 | 104.2 | 464 | 1.0 cc. 4 M | 0.04 | 74.1 | 322 |
| 2.0 | 0.08 | 119.9 | 537 | 2.5 | 0.10 | 77.5 | 341 |
| 4.0 | 0.16 | 130.0 | 584 | 5.0 | 0.20 | 90.7 | 408 |
| 6.0 | 0.24 | 147.8 | 669 | 10.0 | 0.40 | 107.7 | 482 |
| 10.0 | 0.40 | 144.2 | 650 | 20.0 | 0.80 | 109.5 | 491 |
| 13.—Potassium chloride. (0.07 mg. Malt Amylase 118; 100 cc. neutral 2% Starch 6 in each case.) | | | | 16.—Potassium nitrate. (Same enzyme and starch as above.) | | | |
| None | 0.00 | 64.6 | 286 | None | 0.00 | 62.2 | 272 |
| 1.0 cc. 4 M | 0.04 | 92.7 | 414 | 2.0 cc. 2.5 M | 0.05 | 68.0 | 300 |
| 2.0 | 0.08 | 117.8 | 528 | 5.0 | 0.105 | 79.3 | 350 |
| 4.0 | 0.16 | 140.5 | 636 | 10.0 | 0.25 | 98.0 | 437 |
| 6.0 | 0.24 | 139.5 | 632 | 20.0 | 0.5 | 126.9 | 570 |
| 10.0 | 0.40 | 159.7 | 726 | 30.0 | 0.75 | 110.8 | 496 |

¹ THIS JOURNAL, 17, 587 (1895).

² The indicated amounts of reagent solutions are included within the final volume of 100 cc. which, as explained above, was the same in every case.

TABLE II.—EFFECT OF SALTS ON SACCHAROGENIC ACTIVITY—(Continued).

| Amount of salt added. ¹ | Molar concent. of salt. | Reduction in mg. of Cu ₂ O. | Power. | Amount of salt added. ¹ | Molar concent. of salt. | Reduction in mg. of Cu ₂ O. | Power. |
|---|-------------------------|--|--------|---|-------------------------|--|--------|
| 17.—Sodium sulfate. (0.07 mg. Malt Amylase; 100 cc. neutral 2% Starch 6 in each case.) | | | | 19.—Primary sodium phosphate. (0.07 mg. Malt Amylase; 100 cc. 2% Starch 6 in each case.) | | | |
| First series. (Prep. 118.) | | | | First series. (Prep. 111A; Starch 6.) | | | |
| None | 0.00 | 65.4 | 287 | None | 0.00 | 51.7 | 243 |
| 1.0 cc. 0.33 <i>M</i> | 0.0033 | 70.4 | 309 | 2.5 cc. 0.2 <i>M</i> | 0.005 | 111.5 | 500 |
| 5.0 | 0.0166 | 84.2 | 373 | 5.0 | 0.01 | 125.2 | 561 |
| 10.0 | 0.0333 | 99.5 | 446 | 10.0 | 0.02 | 145.4 | 655 |
| 20.0 | 0.0666 | 118.5 | 533 | 20.0 | 0.04 | 152.0 | 688 |
| 30.0 | 0.1000 | 139.7 | 631 | 30.0 | 0.06 | 159.5 | 726 |
| Second series. (Prep. 111A.) | | | | Second series. (Prep. 118; Starch 2b.) | | | |
| None | 0.00 | 55.8 | 245 | None | 0.00 | 6.9 | 29 |
| 30.0 | 0.1 | 125.2 | 561 | 10.0 cc. 0.2 <i>M</i> | 0.02 | 163.2 | 740 |
| 40.0 | 0.134 | 141.6 | 641 | 20.0 | 0.04 | 188.7 | 865 |
| 50.0 | 0.167 | 140.9 | 636 | 30.0 | 0.06 | 202.6 | 934 |
| 18.—Potassium sulfate. (0.07 mg. Malt Amylase; 100 cc. neutral 2% Starch 6 in each case.) | | | | 20.—Primary potassium phosphate. First series. (0.2 mg. Malt Amylase 43B; 100 cc. 2% Starch 2a in each case.) | | | |
| First series. (Prep. 118.) | | | | None | 0.00 | 106.9 | 167 |
| None | 0.00 | 65.5 | 290 | 25.0 cc. 0.2 <i>M</i> | 0.05 | 202.1 | 325 |
| 1.0 cc. 0.67 <i>M</i> | 0.0067 | 80.3 | 354 | 30.0 | 0.06 | 200.5 | 323 |
| 5.0 | 0.0334 | 109.1 | 501 | Second series. (0.07 mg. Malt 111A; 100 cc. 2% Starch 6 in each case.) | | | |
| 10.0 | 0.0668 | 135.3 | 608 | None | 0.00 | 57.3 | 249 |
| 20.0 | 0.134 | 156.8 | 712 | 5.0 cc. 0.2 <i>M</i> | 0.01 | 130.4 | 584 |
| 30.0 | 0.2 | 166.0 | 754 | 10.0 | 0.02 | 143.7 | 650 |
| Second series. (Prep. 111A.) | | | | 30.0 | 0.06 | 152.8 | 693 |
| None | 0.00 | 55.8 | 245 | Third series. (0.07 mg. Malt 118; 100 cc. 2% Starch 6 in each case.) | | | |
| 30.0 | 0.2 | 153.1 | 693 | None | 0.00 | 65.3 | 285 |
| 40.0 | 0.268 | 163.6 | 745 | 30.0 cc. 0.2 <i>M</i> | 0.06 | 185.8 | 860 |

In the case of the primary sodium phosphate it will be seen that the optimum activities observed were at 0.06 *M*.

Since, as already explained, the experimental method did not permit of carrying the comparison to concentrations higher than 0.06 *M*, the possibility of activation still higher than shown at that point is not excluded, but the form of curve obtained on plotting the results makes it probable that approximately the optimum activation is reached at 0.06 *M*.

Measurements of hydrogen-ion concentration in 0.06 *M* sodium and potassium acid phosphates gave Sørensen exponents of 4.6 and 4.2, respectively.

¹ The indicated amounts of reagent solutions are included within the final volume of 100 cc. which, as explained above, was the same in every case.

The Influence of Acids and Salts upon the Amyloclastic Action.

Determination of Amyloclastic Power.—For determination of amyloclastic power of the amylase a procedure based upon the method of Wohlgemuth¹ was used. This procedure is as follows: Forty-two test tubes very carefully cleaned and dried are placed in a special wire frame or basket and the whole set in a bath of ice water. Then 2.5 cc. of 2% starch solution are carefully measured into each of the tubes by means of a buret which has a very long delivery tip reaching to the bottom of the test tube, thus avoiding the lodging of any of the solution on the sides of the tube.

To the starch solution in the tubes the solution of activating agent is added in the same manner, then enough pure water is added to each tube to make the final volume exactly 5 cc. and the concentration of starch 1%. After each addition of activating agent and water the tube is shaken to mix thoroughly. Very carefully measured portions of enzyme solution are now introduced into each tube and the tube agitated to ensure a perfect mixture. No reaction takes place because the solutions are kept cold by the ice water in which the basket of tubes rests.

The basket of tubes is transferred from the ice water to the constant temperature 40° bath and at the expiration of 30 min. is taken out and placed in the ice water to stop the action. Thus the tubes are subjected to an average temperature of 40° for 30 min. After a few minutes 0.1 cc. of 0.1 *N* iodine in potassium iodide solution is added to each tube. It is extremely important that the same amount of iodine solution be added

TABLE III.—EFFECT OF ACETIC ACID ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 118; Starch 6.)

| Concentration of acid. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|------------|-------------|-------------|------------|---------------|
| | 0.028. | 0.035. | 0.042. | 0.049. | 0.056 | 0.063. |
| | Red-violet | *Red | Red | Orange-red | Orange | Orange |
| 143,000 | (heavy) | | | | | (faint) |
| 0.00008 <i>N</i> | Violet-red | *Red | Orange-red | Red-orange | Orange | Yellow-orange |
| 143,000 | | | | | | (faint) |
| 0.00016 <i>N</i> | Violet-red | *Red | Orange-red | Red-orange | Orange | Yellow-orange |
| 143,000 | | (light) | | | (faint) | (faint) |
| 0.00024 <i>N</i> | Violet-red | *Red | Orange-red | Orange | Orange | Yellow-orange |
| 143,000 | | | | | | |
| 0.00032 <i>N</i> | Violet-red | *Red | Orange-red | Red-orange | Orange | Orange |
| 143,000 | | | | | | (faint) |
| 0.00040 <i>N</i> | Violet-red | *Red | Red (light) | Red-orange | Orange | Orange |
| 143,000 | | | | | | (faint) |
| 0.00080 <i>N</i> | Violet | Violet-red | *Red | Red (light) | Orange-red | Red-orange |
| 119,000 | | | | | | |

* The asterisk designates the end point tube.

¹ *Biochem. Z.*, 9, 1 (1908).

to each tube since variation in the iodine concentration will give serious differences in color value. In this laboratory a dropping bottle is used that delivers drops of 0.1 cc. volume. About 20 cc. of distilled water are then poured into each tube, filling it within about 2 cm. of the top, and the contents thoroughly mixed. Each given set of tubes (containing the same amount of added reagent) is then observed for the end point, *i. e.*, the tube of lowest enzyme concentration which shows none of the familiar blue or violet color due to starch, and the weight of 1% starch solution, 5000 mg., is divided by the weight in milligrams of enzyme present to give the numerical value of the amylolytic power of the enzyme.

TABLE IV.—EFFECT OF PROPIONIC ACID ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 118; Starch 6.)

| Concentration of acid. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|------------|------------|------------|------------|------------|
| | 0.028. | 0.035. | 0.042. | 0.049. | 0.056. | 0.063. |
| | Red-violet | *Red | Orange-red | Red-orange | Red-orange | Orange |
| 143,000 | | | | | | |
| 0.00008 <i>N</i> | Violet-red | *Red | Orange-red | Red-orange | Orange | Orange |
| 143,000 | | | | | | |
| 0.00016 <i>N</i> | Violet-red | *Red | Orange-red | Red-orange | Orange | Orange |
| 143,000 | | | | | | |
| 0.00024 <i>N</i> | Violet-red | *Red | Orange-red | Red-orange | Orange | Orange |
| 143,000 | | | | | | |
| 0.00032 <i>N</i> | Violet-red | *Red | Orange-red | Red-orange | Red-orange | Orange |
| 143,000 | | | | | | |
| 0.00040 <i>N</i> | Red-violet | *Red | Orange-red | Orange-red | Orange | Orange |
| 143,000 | | | | | | |
| 0.00080 <i>N</i> | Violet | Violet-red | *Red | Red | Orange-red | Orange-red |
| 119,000 | | | | | | |

TABLE V.—EFFECT OF PHOSPHORIC ACID ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 111A; Starch 6.)

| Concentration of acid. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|-------------|------------|--------------|------------|---------------|
| | 0.020. | 0.024. | 0.028. | 0.032. | 0.036. | 0.040. |
| | Violet | Violet-red | Violet-red | *Red (light) | Orange-red | Red-orange |
| 157,000 | | | (light) | | | |
| 0.00008 <i>N</i> | Red-violet | Violet-red | *Red | Orange-red | Red-orange | Orange |
| 179,000 | | | | | | |
| 0.00016 <i>N</i> | Violet-red | *Red | Orange-red | Red-orange | Orange | Yellow-orange |
| 208,000 | (heavy) | | | | | |
| 0.00024 <i>N</i> | Violet-red | *Red | Orange-red | Red-orange | Orange | Yellow-orange |
| 208,000 | | | | | | |
| 0.00032 <i>N</i> | Red-violet | Violet-red | *Red | Red-orange | Orange | Orange |
| 179,000 | | | (light) | | | |
| 0.0004 <i>N</i> | Red-violet | Violet-red | *Red | Orange-red | Orange-red | Red-orange |
| 179,000 | (heavy) | (heavy) | | | | |
| 0.0006 <i>N</i> | Blue | Blue-violet | Red-violet | Violet-red | Violet-red | *Red |
| 125,000 | | | | | | |

* The asterisk designates the end point tube.

For example, six portions of enzyme solution containing 0.2 mg. per cc. were measured into six tubes as follows: 0.3 cc., 0.4 cc., 0.5 cc., 0.6 cc., 0.7 cc., and 0.8 cc. After carrying out the procedure just described the following colors were obtained: 1, Blue; 2, Blue; 3, Red-Violet; 4, Violet-Red; 5, Red; 6, Orange-Red. The Wohlgemuth end point was reached in tube No. 5. This tube contained 0.7 cc. or 0.14 mg. of enzyme, therefore the power for 30 min. digestion at 40° ($D_{30'}^{40^\circ}$) is equal to $5000/0.14 = 35,714$ or in round numbers 35,700.

TABLE VI.—EFFECT OF HYDROCHLORIC ACID ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 111A; Starch 6.)

| Concentration of acid. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|-------------------|--------------------|-------------|------------|-------------------|
| | 0.020. | 0.024. | 0.028. | 0.032. | 0.036. | 0.040. |
| | Violet | Red-violet | †Violet-red (pale) | †Orange-red | Red-orange | Red-orange |
| 167,000 | | | | | | |
| 0.00004 <i>N</i> | Violet | Violet-red | *Red | Orange-red | Orange | Orange |
| 179,000 | | | | | | |
| 0.00008 <i>N</i> | Violet-red | Violet-red (pale) | *Red (light) | Red-orange | Orange | Yellow-orange |
| 179,000 | | | | | | |
| 0.00012 <i>N</i> | Red-violet | Violet-red | †Violet-red (pale) | †Red-orange | Orange | Orange |
| 167,000 | | | | | | |
| 0.00014 <i>N</i> | Violet | Violet-red | Violet-red | *Red | Orange-red | Red-orange |
| 157,000 | | | | | | |
| 0.00016 <i>N</i> | Blue | Red-violet | Violet-red | *Red | Red (pale) | Red (pale) |
| 157,000 | | | | | | |
| 0.00020 <i>N</i> | Blue | Blue | Violet | Red-violet | Red-violet | Violet-red (pale) |
| 113,000 | | | | | | |

TABLE VII.—EFFECT OF NITRIC ACID ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 111A; Starch 6.)

| Concentration of acid. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|------------|-------------|--------------------|--------------------|---------------|
| | 0.024. | 0.028. | 0.032. | 0.036. | 0.040. | 0.044. |
| | Red-violet (heavy) | Violet-red | *Red | Orange-red | Red-orange | Orange |
| 157,000 | | | | | | |
| 0.00004 <i>N</i> | Violet-red (heavy) | *Red | Red (light) | Orange-red | Red-orange | Orange |
| 179,000 | | | | | | |
| 0.00008 <i>N</i> | Violet-red | *Red | Red-orange | Red-orange | Orange | Yellow-orange |
| 179,000 | | | | | | |
| 0.00012 <i>N</i> | Violet-red (heavy) | *Red | Red | Red (light) | Orange-red | Red-orange |
| 179,000 | | | | | | |
| 0.00014 <i>N</i> | Blue-violet | Violet-red | *Red | Red (light) | Orange-red | Orange-red |
| 157,000 | | | | | | |
| 0.00016 <i>N</i> | Blue | Red-violet | Violet-red | Violet-red (faint) | *Red (light) | Orange-red |
| 125,000 | | | | | | |
| 0.0002 <i>N</i> | Blue | Blue | Violet | Red-violet (heavy) | Violet-red (heavy) | Violet-red |
| less than 113,000 | | | | | | |

* The asterisk designates the end point tube.

† In these cases the quality of colors was such that the end point was judged to be half-way between the two tubes.

In testing the effect of any reagent to be examined, six or seven tubes are ordinarily tested with the same amount of reagent but with varying amounts of enzyme solution. Seven or six such sets of tests, each set containing a different amount of reagent, are made for every reagent to be examined. Hence each set of tubes contains the same concentration of reagent whose effect is to be determined, but differing concentrations of enzyme while the several sets of tubes differ from each other in that they contain varying concentrations of activating agent.

TABLE VIII.—EFFECT OF SULFURIC ACID ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 111A; Starch 6.)

| Concentration of acid. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|--------------------|--------------------|--------------------|--------------------|------------|
| | 0.024. | 0.028. | 0.032. | 0.036. | 0.040. | 0.044. |
| | Violet | Violet-red | *Red | Orange-red | Orange-red | Red-orange |
| 157,000 | | | | | | (faint) |
| 0.00004 <i>N</i> | Red-violet | Violet-red | *Red | Orange-red | Orange-red | Red-orange |
| 157,000 | | | | | | (faint) |
| 0.00008 <i>N</i> | Violet-red | *Red | Red | Orange-red | Red-orange | Red-orange |
| 179,000 | | | | | | (faint) |
| 0.00012 <i>N</i> | Red-violet | †Violet-red | †Orange-Red | Orange-red | Red-orange | Red-orange |
| 167,000 | | | | | | (faint) |
| 0.00014 <i>N</i> | Violet | Violet-red (heavy) | *Red | Red (light) | Red (light) | Orange-red |
| 157,000 | | | | | | |
| 0.00016 <i>N</i> | Violet (heavy) | Violet-red (heavy) | Violet-red (heavy) | *Red (dark) | Red | Red |
| 139,000 | | | | | | |
| 0.0002 <i>N</i> | Blue | Blue | Violet (heavy) | Violet-red (heavy) | Violet-red (heavy) | Violet-red |
| less than 113,000 | | | | | | |

TABLE IX.—EFFECT OF SODIUM CHLORIDE ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 118; Starch 6.)

| Concentration of salt. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|-------------|------------|------------|------------|------------|
| | 0.021. | 0.028. | 0.035. | 0.042. | 0.049. | 0.056. |
| | Blue | Violet-red | *Red | Orange-red | Red-orange | Orange |
| 143,000 | | | | | | |
| 0.08 <i>M</i> | Blue | Violet-red | *Red | Orange-red | Red-orange | Orange |
| 143,000 | | | | | | |
| 0.16 <i>M</i> | Violet | †Violet-red | †Red | Orange-red | Orange | Orange |
| 158,700 | | | | | | |
| 0.32 <i>M</i> | | Violet-red | *Red | Red | Red-orange | Orange |
| 143,000 | | | | | | |
| 0.48 <i>M</i> | | | Violet-red | *Red | Orange-red | Orange-red |
| 119,000 | | | | | | |
| 0.64 <i>M</i> | | | Violet-red | *Red | Red | Orange-red |
| 119,000 | | | | | | |
| 0.8 <i>M</i> | | | | Violet-red | *Red | Orange-red |
| 102,000 | | | | | | |

* End point was found with 0.5 mg. enzyme.

† In these cases the quality of colors was such that the end point was judged to be half-way between the two tubes.

In the tables which follow the "power," *i. e.*, the numerical result calculated as above from the amount of enzyme preparation required to carry the digestion to the Wohlgemuth end point, is given in the first column with the concentration of reagent, while the columns following show the colors¹ obtained in each test of the set. One reason for recording all of these colors is to facilitate comparison with somewhat analogous

TABLE X.—EFFECT OF POTASSIUM CHLORIDE ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 43B; Starch 6.)

| Concentration of salt. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|-------------|-------------|-------------|------------|------------|
| | 0.6. | 0.8. | 0.9. | 1.0 | 1.2. | 1.4. |
| | Violet-red | Violet-red | Violet-red | *Red | Orange-red | |
| 54,300 | | (light) | (light) | (light) | | |
| 0.008 M | Red-violet | *Red | Red (light) | Red-orange | | |
| 62,500 | | | | | | |
| 0.08 M | Violet-red | *Red | | | Orange | |
| 62,500 | | | | | (light) | |
| 0.16 M | Violet-red | †Violet-red | †Red- | Red-orange | Red-orange | |
| 59,500 | | (light) | orange | | | |
| 0.32 M | Blue | Violet | *Red | Orange | Orange | |
| 54,300 | | | | | | |
| 0.4 M | Blue | Blue-violet | | †Violet-red | †Red- | Yellow- |
| 49,000 | | | | | orange | Orange |
| 0.8 M | Blue | Blue | | Blue | Blue | Violet-red |
| 35,200 ² | | | | | | |

TABLE XI.—EFFECT OF SODIUM NITRATE ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 118; Starch 6.)

| Concentration of salt. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|-------------|------------|-------------|------------|---------|
| | 0.014. | 0.021. | 0.028. | 0.035. | 0.042. | 0.049. |
| | Blue | Red-violet | Violet-red | *Red | Orange | Orange |
| 143,000 | | | | | | |
| 0.08 M | Blue | Red-violet | *Red | Red (light) | Red-orange | Orange |
| 179,000 | | | | | | |
| 0.16 M | Blue | Red-violet | *Red | Red (light) | Orange | Yellow- |
| 179,000 | | | | | | orange |
| 0.32 M | Blue | Violet | Violet-red | *Red | Red | Orange |
| 143,000 | | | | | | |
| 0.48 M | Blue | Violet | Violet-red | *Red | Red | Orange |
| 143,000 | | | (dark) | (dark) | | |
| 0.64 M | Blue | Violet | Violet-red | *Red | Red | Red |
| 143,000 | | (dark) | (dark) | (dark) | | |
| 0.8 M | Blue | Blue-violet | Red-violet | Violet-red | *Red | Red |
| 119,000 | | | | | (dark) | |

† In these cases the quality of colors was such that the end point was judged to be half-way between the two tubes.

¹ The terminology used in describing the colors is that of the Milton Bradley Standard Color Chart as given by Mullikin in his "Identification of Pure Organic Compounds."

² End point was found with 1.5 mg. enzyme.

studies of other amylases in which the results are similarly expressed, such as those of Long and Johnson.¹

Another reason is that to judge of the amyloclastic activity of a purified preparation of malt amylase on the basis of the Wohlgemuth end point exclusively is likely to be misleading because of the relative persistence of material giving a slight blue or violet iodine reaction when starch is digested by preparations of this character. Thus in the case of the example given above, while the Wohlgemuth end point was found in tube 5 containing 0.7 cc. of enzyme solution or 0.14 mg. of the enzyme preparation, yet in tube 3 having 0.5 cc. or 0.10 mg. there was no

TABLE XII.—EFFECT OF POTASSIUM NITRATE ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 118; Starch 6.)

| Concentration of salt. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|-------------|------------|------------|------------|------------|
| | 0.014. | 0.021. | 0.028. | 0.035. | 0.042. | 0.049. |
| | Blue | Blue-violet | Violet-red | *Red | Orange-red | Red-orange |
| 143,000 | | | | | | |
| 0.05 M | Blue | Blue-violet | Violet-red | *Red | Red-orange | Orange |
| 143,000 | | | | | | |
| 0.1 M | Blue | Violet | Violet-red | *Red | Red-orange | Orange |
| 143,000+ | | | | (light) | | |
| 0.2 M | Blue | Violet | *Red | Orange-red | Red-orange | Orange |
| 179,000 | | | | | | |
| 0.4 M | Blue | Violet | Violet-red | *Red | Red-orange | Orange |
| 143,000+ | | | (light) | (light) | | |
| 0.5 M | Blue | Violet | Violet-red | *Red | Orange-red | Red-orange |
| 143,000 | | | | | | |
| 0.75 M | Blue | Blue-violet | Violet | Violet-red | *Red | Orange-red |
| 119,000 | | | | | | |

TABLE XIII.—EFFECT OF SODIUM SULFATE ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 111A; Starch 6.)

| Concentration of salt. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|------------|------------|------------|------------|------------|
| | 0.0175. | 0.0210. | 0.0245. | 0.0280. | 0.0315. | 0.0350. |
| | Blue-violet | Violet | Red-violet | Violet-red | *Red | Orange-red |
| 160,000 | | | | | | |
| 0.0133 M | Blue-violet | Violet | Red-violet | Violet-red | *Red | Red-orange |
| 160,000 | | | | | | |
| 0.0267 M | Violet | Red-violet | Violet-red | *Red | Red | Red-orange |
| 180,000 | | | | | | |
| 0.04 M | Violet | Red-violet | Violet-red | *Red | Orange-red | Red-orange |
| 180,000 | | | | | | |
| 0.053 M | Violet | Red-violet | Violet-red | *Red | Red-orange | Red-orange |
| 180,000+ | | | (pale) | (light) | | |
| 0.067 M | Violet | Red-violet | Violet-red | *Red | Orange-red | Red-orange |
| 180,000 | | | | | | |
| 0.133 M | Blue-violet | Red-violet | Violet-red | *Red | Orange-red | Red-orange |
| 180,000 | | | | | | |

* The asterisk designates the end point tube.

¹ THIS JOURNAL, 35, 895 (1913).

typical starch-iodine blue. If this were taken as the end point the power of the enzyme would be 50,000 or about 40% higher. Examination of the color readings in Tables XVI will show that in many, if not in most, cases the amount of enzyme required to carry the digestion to the "red" end point is one-third to one-half greater than that which carries it to the disappearance of the typical "blue." In view of the fact that this point has been dealt with in a recent paper from this laboratory,¹ it need not be further discussed here, nor in connection with the tables which are given:

There is no apparent activation of the amylolytic action by the addition of acetic acid, but beyond the concentration at which the optimum saccharogenic action was obtained there is depression of the amylolytic as of the saccharogenic power.

The results in Table IV are closely analogous to those just noted in the case of acetic acid.

with phosphoric acid there is a distinct activation. It will be noted that the optimum concentration of phosphoric acid for amylolytic action as judged by the Wohlgemuth end point is much lower than the optimum for saccharogenic activity. Attention may also be called to the persistence of colors intermediate between blue and red which has already been referred to at the top of the page.

For HCl, as in the case of phosphoric acid, the optimum is much lower than for saccharogenic action and the concentration which gives optimum saccharogenic action has a distinct inhibitory influence upon the amylolytic action as measured by this method. The unsatisfactory nature of the end point is again apparent.

What has been said of the influence of hydrochloric acid upon amylolytic action will be seen to apply also to nitric and sulfuric acids.

TABLE XIV.—EFFECT OF POTASSIUM SULFATE ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 111A; Starch 6.)

| Concentration of salt. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|-------------|------------|-------------|------------|------------|
| | 0.0175. | 0.0210. | 0.0245. | 0.0280. | 0.0315. | 0.0350. |
| | Violet-blue | Blue-violet | Red-violet | Violet-red | *Red | Orange-red |
| 160,000 | | | | | | |
| 0.0267 <i>M</i> | Violet-blue | Violet | Violet-red | *Red | Orange-red | Red-orange |
| 180,000 | | | | | | |
| 0.0534 <i>M</i> | Violet | Red-violet | Violet-red | *Red | Orange-red | Red-orange |
| 180,000 | (dark) | | | | | |
| 0.08 <i>M</i> | Blue-violet | Red-violet | *Red | Red (light) | Orange-red | Red-orange |
| 204,000 | | | | | | |
| 0.107 <i>M</i> | Violet | Red-violet | *Red | Red (light) | Orange-red | Red-orange |
| 204,000 | (dark) | | | | | |
| 0.1335 <i>M</i> | Blue-violet | Red-violet | Violet-red | *Red | Orange-red | Red-orange |
| 180,000 | | | | (light) | | |

* The asterisk designates the end point tube.

¹ THIS JOURNAL, 35, 1784 (1913).

With the chlorides, nitrates, and sulfates of sodium and potassium, as with the corresponding acids, the optimum concentrations are much lower for the (apparent) amylolytic than for the saccharogenic action.

TABLE XV.—EFFECT OF PRIMARY SODIUM PHOSPHATE ON AMYLOCLASTIC ACTION.
(Malt Amylase preparation 118; Starch 6.)

| Concentration of salt. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|--------------|------------|---------------|---------------|---------------|
| | 0.028. | 0.035. | 0.042. | 0.049. | 0.056. | 0.063. |
| | Violet | *Red | Orange-red | Red-orange | Orange | Yellow-orange |
| 143,000 | | | | | | |
| 0.008 M | Violet-red | *Red | Orange-red | Red-orange | Orange | Yellow-orange |
| 143,000+ | | | | | | |
| 0.016 M | †Violet-red | †Red | Orange-red | Orange | Yellow-orange | Orange-yellow |
| 159,000 | (light) | (light) | (light) | | | |
| 0.024 M | †Violet-red | †Red (light) | | Yellow-orange | Yellow-orange | Orange-yellow |
| 159,000 | | | | | (faint) | |
| 0.032 M | †Violet-red | †Red | Orange-red | Orange | Yellow-orange | Orange-yellow |
| 159,000 | | (light) | (faint) | (faint) | | |
| 0.04 M | Violet-red | *Red | Orange-red | Orange | Yellow-orange | Orange-yellow |
| 143,000+ | | | | | | |
| 0.08 M | Violet-red | *Red | Orange-red | Red-orange | Orange | Yellow-orange |
| 143,000 | | | | | | |

TABLE XVI.—EFFECT OF PRIMARY POTASSIUM PHOSPHATE ON AMYLOCLASTIC ACTION.

(Malt Amylase preparation 43B; Starch 6.)

| Concentration of salt. Power. | Weights of enzyme in mg. | | | | | |
|----------------------------------|--------------------------|------------|------------|------------|-------------------|---------------|
| | 0.4. | 0.6. | 0.8. | 0.9. | 1.0. | 1.2. |
| | Blue | Blue | Violet-red | *Red | Orange-red | Red-orange |
| 55,600 | | | | | | |
| 0.008 M | Blue | Violet-red | *Red | | Orange | Yellow-orange |
| 62,500 | | | (light) | | | |
| 0.02 M | Blue | Red-violet | *Red | | Orange-red | Orange |
| 62,500 | | | (light) | | | (light) |
| 0.04 M | Blue | Blue | Red-violet | Violet-red | Violet-red | *Red |
| 41,700 | | | | | | |
| 0.06 M | 0.6. | 0.8. | 1.0. | 1.2. | 1.4. | 1.6. |
| 35,700 | Blue | Red-violet | Violet-red | Violet-red | *Red | Orange-red |
| 0.08 M | 0.8. | 1.0. | 1.2. | 1.4. | 1.6. | 1.8. |
| 29,400 | Violet | Violet | Red-violet | Violet-red | Violet-red | *Red |
| 0.1 M | 1.0. | 1.2. | 1.4. | 1.6. | 2.0. | 2.4. |
| 22,200 | Blue-violet | Red-violet | Violet-red | Violet-red | Violet-red (pale) | *Red (pale) |

* The asterisk designates the end point tube.

† In these cases the quality of colors was such that the end point was judged to be half-way between the two tubes.

In the case of the acid phosphates, as of the free acids and the neutral salts, optimum amylolytic activities, as measured by the Wohlgemuth

method, are reached at concentrations much lower than those which give optimum saccharogenic action, and the latter concentrations distinctly depress the amylolytic action.

Summary.

The effects of acetic, propionic, phosphoric, hydrochloric, nitric and sulfuric acids, and the chlorides, nitrates, sulfates and primary phosphates of sodium and potassium are described. Special reference is made to the determination of concentrations favoring optimum activity of malt amylase.

Previous studies made in this laboratory, showing that the measurement of amylolytic action by determining the conditions under which the starch-iodine end point occurs, gives with purified malt amylase results which are of little value compared with those obtained by the measurement of the saccharogenic action, have been confirmed. Full data of the amylolytic action have been given in the foregoing text. The conclusions which follow refer, except as otherwise explained, to the saccharogenic action.

Special attention has been given to the purification of the amylase preparations, the starch, the activating agents, and the water used. While we have not, as in the case of pancreatic amylase, observed any case of complete inactivation of the enzyme through deficiency of electrolyte alone, it is plain that the activities shown by purified materials in the absence of added electrolytes are to be regarded as abnormally low.

All of the electrolytes above mentioned increased the activity of malt amylase. The activities observed at the optimum concentrations of these different activating electrolytes varied from less than double to more than thirty-fold the corresponding activities in the absence of the electrolyte; depending chiefly upon the purity of the enzyme preparation and the starch employed. In comparing the activating influence of different electrolytes more weight should be attached to the maximum saccharogenic power demonstrated in the case of each electrolyte by the same enzyme preparation than to the increase of power above that shown when no electrolyte was added.

In those cases in which the use of the same enzyme permits comparison of results obtained in different series of experiments, it appears that the acids had a greater activating influence than the neutral salts, while the acid phosphates of sodium and potassium gave as high an activation as did any of the free acids. The main object held in view in the arrangement of the experiments was, however, not to compare the acids and salts with each other but to establish the optimum concentration of each of the activating agents considered separately, and particularly the optimum of each acid in terms of hydrogen-ion concentration.

The weak acids (acetic, propionic, phosphoric), the strong acids (hydro-

chloric, nitric, sulfuric), and the acid phosphates of sodium and potassium, all showed optimum activation in those concentrations which have essentially the same actual acidity. This optimum hydrogen-ion concentration, as determined by the electrometric method and expressed by Sørensen's exponent, was found in each case between the limits p_H^+ 4.2 to 4.6.

Additions of free acid in concentrations greater than the optimum have a marked depressing influence upon the activity of the enzyme which is naturally more striking in the case of the stronger acids. Acetic and propionic acids in quantities ten times the optimum decrease the activity about one-half; hydrochloric, nitric and sulfuric acids reduce the activity more than one-half when present in concentrations two and one-half times the optimum, while in presence of five to eight times the optimum of these strong acids the enzyme action was almost entirely destroyed. In determining the diastatic power of malt preparations, acid phosphate may conveniently be used to ensure activation with little danger of excessive acidity.

Whether the activating agent be an acid or a salt, the amyloclastic action, as measured by the Wohlgemuth method, reaches an optimum at a concentration of the activating agent much below that which gives optimum saccharogenic action. Those concentrations which give the optimum saccharogenic activity are so far above the optimum for amyloclastic action (Wohlgemuth method) as to show a distinct inhibitory influence.

We desire to express our indebtedness to the Carnegie Institution of Washington for use of malt amylase preparations which had been purified in connection with investigations conducted by aid of its grants and described in other papers from this laboratory.

For the data given in Tables X and XVI we are indebted to our former associate, Dr. C. F. Hinck.

LABORATORY OF FOOD CHEMISTRY, COLUMBIA UNIVERSITY,
NEW YORK CITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 246.]

STUDIES ON AMYLASES. IX. FURTHER EXPERIMENTS UPON THE PURIFICATION OF MALT AMYLASE.

By H. C. SHERMAN AND M. D. SCHLESINGER.

Received January 25, 1915.

In continuing our experiments upon the purification of malt amylase¹ the operations of precipitation, solution, and dialysis which are involved in the purification process have been studied in some detail, with a view to determining quantitatively the loss of diastatic power at each step and,

¹ THIS JOURNAL, 35, 1617-23 (1913).

if possible, finding means to control these losses so as to secure a definite product of maximum activity.

In fractional precipitation with alcohol the greatest destruction of enzyme usually occurs in the first precipitation. Losses in the final precipitation with alcohol and subsequent drying in partial vacuum were found to be less serious than might be expected from the statements of some previous writers. In general, the largest losses of diastatic power occurred during dialysis, but since dialysis is the best available means of separating certain impurities from the enzyme it has not been found practicable to eliminate this step from our purification process. That the loss of activity which occurs during dialysis is not due in any large measure to the passage of the enzyme as such through the dialyzing membrane is shown by examination of the dialysate for diastatic power.¹

Osborne's theory of the chemical nature of the enzyme² affords a possible explanation. If, as Osborne suggested and as our experiments also indicate, the enzyme is a compound of an albumin with a proteose or peptone, which compound is hydrolyzed on heating in water, it would seem probable that a fraction of the enzyme would be hydrolyzed in water solution even at low temperatures. The removal, then, of one of the products of hydrolysis (*i. e.*, the proteose or peptone) by dialysis would result in a further hydrolysis of the enzyme and loss of diastatic power in the solution undergoing dialysis without any accumulation of enzyme in the dialysate. Quantitative experiments upon the loss of activity in dialyzed solutions of the purified enzyme, as contrasted with duplicate solutions kept at the same temperature but not submitted to dialysis, will be described in our next paper.

From the temperature coefficient of such hydrolytic reactions and the decreasing ionization of water on cooling, the hypothesis that the loss of activity during dialysis is chiefly due to hydrolytic destruction of the enzyme leads one to expect, what has now been fully established in our experience, that when the dialysis is conducted at ice-box temperature the loss of diastatic power is much diminished while the removal of impurities through the membrane is but little retarded.

Thus, notwithstanding the relative stability of malt amylase solutions in ordinary conditions at room temperature, it is important that the dialysis of such solutions for the removal of impurities be conducted at lower temperature.

As starting material in many of our recent purification experiments we

¹ In a considerable proportion of the cases tested, the dialysate shows some diastatic activity. As this is not only small in comparison with the total loss during dialysis but also very irregular, it is uncertain whether it should be attributed to anything more than imperceptible defects in the membrane.

² THIS JOURNAL, 17, 587-603 (1895); 18, 536-542 (1896).

have used a concentrated malt extract made¹ by evaporating an infusion of pale malt *in vacuo* on a commercial scale, with stirring to prevent the solution from being heated above 40° in contact with the warming surface. Two such products were used.

Extract No. 1 had a specific gravity of 1.27 and contained 7% of alcohol as a preservative. This concentrated extract had been found capable of forming 17.6 times its weight of maltose from a surplus of 3% arrowroot starch paste in 30 minutes at 37.5°.

Extract No. 2 was from the same malt infusion as the above but was still further concentrated *in vacuo* to a specific gravity of 1.39. It contained only 4% of alcohol as preservative and had been found able to produce 23 times its weight of maltose in 30 minutes under the conditions just given in describing Extract No. 1.

The following illustrates the purification method which we have usually employed when starting with such extracts: One liter of the concentrated malt extract is divided into twenty equal portions, each of which is placed in a collodion sac of 500 cc. capacity. The twenty sacs are suspended in 30 liters of water in an ice-jacketed metal tank, the dialysate being maintained at a temperature of 5–10° and allowed to dialyze for 24 hours. In sufficiently cool weather the dialysate is slowly but constantly renewed by means of a current of tapwater running at the rate of 800 cc. per minute; when the tapwater is too warm to permit the use of a constant stream, the dialysate is changed two or three times during the twenty-four hours. At the end of this dialysis the sacs always contain a deposit of material which has precipitated with the removal of dialyzable substances from the solution. This insoluble material, which is without diastatic power, is separated by decantation (with the aid of the centrifuge if necessary) and rejected. To the clear solution from the sacs (which in this case had increased to about three times its original volume) crystallized ammonium sulfate is added in the proportion of 45 g. to 100 cc., the solution being kept in an ice-bath and stirred almost continuously until the crystals have dissolved (usually about 15 minutes); the precipitate produced by ammonium sulfate is then settled by means of the centrifuge, the liquid decanted and rejected, and the precipitate dissolved in 500 to 600 cc. cold water. This solution is divided between four 500 cc. collodion sacs and dialyzed as before for about twenty hours, again decanted from sediment, and then treated with an equal volume of (cold) pure alcohol (99.8%) keeping the temperature below 15°. The material precipitated by this amount of alcohol is separated by means of the centrifuge and rejected.² To the liquid enough more cold alcohol is added to make the alcohol

¹ This extract was kindly prepared for us by Dr. C. Von Egloffstein of the American Diamalt Company to whom, as also to Mr. Kaltenbach and Dr. Schulhof of the same company, we desire to express cordial thanks for courtesies and coöperation.

² This is the material which we have sometimes referred to as "50% precipitate."

content 65% (by volume). The precipitate thus obtained is separated by means of the centrifuge, and dried on a watch-glass in partial vacuum over sulfuric acid in the dark, at a temperature not exceeding 15°.

As will be seen from the abstract of experimental data below, this method of preparation has in several cases been changed for experimental purposes but without resulting in a better product.

The twenty-two preparations made essentially as above described showed diastatic powers ranging from 760 to 1570 (new scale) equivalent to about 1200 to 2350 on Lintner's scale. Thus both the minimum and the average powers are much higher than in the previous year's work; the maximum powers found during the past year are essentially the same as those recorded a year ago.

That a marked advance in the average result did not lead to any increase in the maximum previously observed suggests that the six most active preparations, having powers of 1430 to 1570 (new scale) equivalent to 2150 to 2350 on Lintner's scale, may approximate the maximum activity obtainable by this method of purification. It may also be noted that these products were obtained not only at intervals of several months but also from different materials; 3 of the preparations from kiln-dried pale malt, 1 from green malt, and 2 from the malt extracts described above. Nevertheless it appears probable, for reasons given in this and the following paper, that all the preparations contain inactive albumin in addition to the enzyme itself.

Brief descriptions of the various preparations made during the past year will be given at the end of the paper. *

Our most active preparations, made as above described, contain 15.1–15.3% of nitrogen in the dry ash-free substance. Osborne's most active preparation, showing diastatic power of 600 Lintner, contained 16.1% nitrogen. His other preparations varied considerably both in power and in nitrogen content.¹ On account of the fact that our determinations of nitrogen were necessarily made upon very small amounts of material, and in view of the differences in nitrogen content among the various preparations described by Osborne, we do not attach any exact quantitative significance to the difference in the apparent percentages of nitrogen, but conclude simply that our preparations have a slightly lower nitrogen content than Osborne's. The principal difference in the methods by which Osborne's product and our own were obtained is that Osborne dialyzed for several days, apparently at the temperature of the room or of tap-water, while we dialyzed for not over forty-four hours in all and at a temperature below 10°. On following Osborne's general method, we obtained a preparation having practically the same nitrogen content and diastatic power as Osborne's most active product. (Our preparation

¹ THIS JOURNAL, 17, 591–99 (1895).

124B with 16.0% of nitrogen and a diastatic power of 660 Lintner.) We attribute this increase of nitrogen content and decrease of power to the prolonged dialysis. In accordance with the theory of the constitution of the enzyme and its hydrolysis in solution outlined above, the higher nitrogen and lower power of the products obtained when dialysis is prolonged are explainable as due to the hydrolysis of the enzyme and the removal of the dialyzable constituent. This dialyzable constituent (proteose or peptone) being a hydrolytic product may be expected to contain a lower percentage of nitrogen than the enzyme as a whole. The corresponding albumin-fraction would thus contain more nitrogen than the enzyme as a whole.

In the case of our preparation IIIB the coagulum contained 16.1% nitrogen and the uncoagulable matter 13.7% nitrogen. While Osborne did not analyze the coagulated albumin obtained on boiling the solution of his enzyme, he has elsewhere¹ given an analysis of malt albumin which shows 16.71% of nitrogen.

It therefore seems probable that the lower nitrogen content and higher diastatic power of our best preparations are both due to the fact that the loss of the peptone or proteose fraction of the enzyme has been minimized by restricting the time and lowering the temperature of the dialysis.

It should be stated, however, that on examining one of our most active preparations (IIIB) we found it to contain slightly more coagulable albumin than did Osborne's most active preparation. It is possible that our methods of purification, while minimizing deterioration and yielding a more active product, may be less efficient than Osborne's in freeing the enzyme from some albumin which accompanies it in the malt. The problem of the chemical nature of the enzyme is discussed further in our next paper.

Abstract of Experimental Data.

Numbers 74¹-76 were preliminary experiments upon a sample of concentrated extract.

Numbers 77-95 were experiments devoted to the study of losses of diastatic power at different steps in purification.

Preparation 96: Malt was extracted with 2½ times its weight of cold water for one-half hour, the extract pressed out and filtered, then precipitated with ammonium sulfate and centrifuged, the precipitate dissolved in cold water and dialyzed in collodion sacs against cold distilled water, the solution then filtered and precipitated with alcohol as described above. Power 1170 (new scale).

Preparations 97, 98, 99² and 101 made in practically the same manner as the preceding, showed powers of 830, 762, 1140, 780, respectively (new scale).

Preparation 102: Malt was extracted with 2½ parts of 10% ammonium sulfate for 1 to 2 hours, pressed and filtered, dialyzed for 23 hours against 10 volumes of cold distilled water with one change of dialysate; freed from sediment by means of the centri-

¹ THIS JOURNAL, 18, 556 (1896).

² Numbers 1-73 are outlined in THIS JOURNAL, 35, 1620-22 (1913).

³ Preparation 100 was lost in drying.

fuge, then precipitated with ammonium sulfate and the preparation completed as described in the early part of this paper. Power 1572 (new scale).

Preparations 103 and 106 made in the same manner as preparation 102 showed powers 1340 and 1110, respectively (new scale).

In **Experiments 104, 105, 107, 109** variations of method were tried without satisfactory result.

Preparation 108: Like 102 except that the original extraction was with 2% neutral lead acetate. Power 790.

Preparation 110: Like 102. Power 1010.

Preparation 111A was made from concentrated malt extract No. 1 as already described in the text. Power 1100; nitrogen in dry, ash-free substance, 15.2%. As the volume of solution became during dialysis too large to be handled as one preparation, a portion was set aside in the ice-box for several hours and then completed in the same way. This product, called **111B**, had a power of 1470¹ and a nitrogen content (in dry, ash-free substance) of 15.2%. The yield of preparation **111 (A and B)** was 2.23 g., obtained from 2 liters of the concentrated malt extract.

Preparation 112: 350 cc. of the same concentrated extract (No. 1) treated as in Preparation **111A** yielded 0.8 g. with power of 900.

Preparations 113 and 114 were made from extract No. 2; otherwise practically duplicates of **111A**; yields 0.22 and 0.23 g. per 100 cc. of original concentrated extract; powers 1020 and 1030, respectively.

Preparations 115 and 116 were made side by side from concentrated extracts Nos. 1 and 2, respectively. The first yielded 0.16 g. per 100 cc. with power of 800; the second, 0.24 g. per 100 cc. with power of 1050.

Preparations 117 and 118 were made from extract No. 2, duplicating the conditions which obtained in the case of preparations **111A** and **111B**, respectively. Yields per 100 cc., 0.14 and 0.24; powers 1455 and 1340, respectively.

Preparation 119: Like 117; yield 0.27 per 100 cc.; power 1185.

Preparations 120-122: Unsuccessful attempts at further purification by reprecipitation and repeated dialysis. Not only was most of the diastatic power destroyed but the material underwent changes which diminished its solubility both in water and in 50% alcohol. Preparation 122, which had been twice precipitated by ammonium sulfate as an additional precaution against retention of carbohydrate, contained 15.2% nitrogen in the dry, ash-free substance and showed a power of 470.

Preparation 123 was made from extract No. 2 in the same manner as Osborne's Precipitate XIII (*THIS JOURNAL*, 18, 539-40 (1896)), except that in dialyzing the temperature was kept below 15° and collodion sacs were used instead of parchment. Yield, 0.13 g. per 100 cc.; power, 105; nitrogen in dry ash-free substance, 15.1%.

Preparations 124A and 124B, made from extract No. 1, were obtained in essentially the same manner in which Osborne obtained his Precipitates III and IV (*THIS JOURNAL*, 17, 593 (1895)). The powers were 330 and 440 (equivalent to about 500 and 660 Lintner) and nitrogen contents (dry, ash-free basis) 15.9 and 16.0%, respectively, thus closely resembling Osborne's Preparation 15 (*Ibid.*, p. 598) from his Precipitate IV.

Preparation 125 was intended as a repetition of 124 and gave products of practically the same power but the yield of the second fraction was too small to permit accurate determination of nitrogen.

We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

LABORATORY OF FOOD CHEMISTRY, COLUMBIA UNIVERSITY,
NEW YORK CITY.

¹ Here, as in all cases, the diastatic power is expressed on the basis of air-dry material.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL,
NEW YORK.]

STUDIES ON ENZYME ACTION. XIII. THE LIPASE OF SOY BEANS.

By K. GEORGE FALK.

Received January 7, 1915.

In continuation of the study of lipolytic activities reported in previous papers,¹ the results obtained in the study of the lipase of soy beans by methods similar to those used in the study of castor bean and duodenal lipases will be given.

Two preparations were used in this work: S.B. I; yellow soy beans, ground, extracted with ether in a Soxhlet apparatus, dried in air, and ground to pass through a 40-mesh sifter; S.B. II; the shells of the soy beans were removed by hand, the kernels ground, extracted with ether, air dried, and ground to pass through a 40-mesh-sifter.

To test the activities of the preparations, the weighed substance with the stated amount of water or of solution in a stoppered Erlenmeyer flask was placed in the incubator at 38–40° with the ester (either 1 cc. ethyl butyrate, denoted by EtBu, or 0.5 cc. glyceryl triacetate, denoted by Triac.) for 24 hours, and then titrated with approximately 0.1 *N* standard NaOH solution, with phenolphthalein as indicator. The final results, corrected for blanks, alone are given, and represent the number of cc. of 0.1 *N* acid formed under the conditions stated by the action of the lipase upon the ester. Toluene was used throughout as antiseptic.

The effect of heating and of drying on the activity of S.B. II was studied and the results are given in Table I. The first column indicates the treatment before testing; the second, the amount of substance used; the third, the loss in weight in grams; the fourth, the percentage loss; and the fifth and sixth the activities of 0.18 g. portions of the treated material in 25 cc. water, except for the first row where the activities of 0.2 g. portions of untreated material are given.

TABLE I.—ACTIVITY OF SOY BEAN LIPASE PREPARATION AFTER DRYING AND HEATING.

| Treatment. | S.B. II. Grams. | Loss in wt. Grams. | Per cent. | Activities. | |
|---|--------------------|-----------------------|-----------|-------------|--------|
| | | | | Et Bu. | Triac. |
| None..... | | | | 0.41 | 2.87 |
| 100–110°, 3 hrs..... | 1.0399 | 0.0894 | 8.60 | 0.20 | 1.54 |
| CaCl ₂ desiccator, 3 days..... | 1.0097 | 0.0685 | 6.78 | 0.36 | 2.78 |
| CaCl ₂ desiccator, 2 days..... | 1.0080 | 0.0587 | 5.82 | | |
| CaCl ₂ desiccator, 2 days more..... | | 0.0635 | 6.30 | | |
| then 100–110°, 3 hrs..... | | 0.0874 | 8.67 | 0.11 | 1.37 |
| P ₂ O ₅ desiccator, 2 days..... | 1.0089 | 0.0864 | 8.56 | | |
| P ₂ O ₅ desiccator, 1 day more..... | | 0.0871 | 8.63 | 0.34 | 2.67 |
| P ₂ O ₅ desiccator, 3 days..... | 1.0070 | 0.0931 | 9.24 | | |
| then 100–110°, 3 hrs..... | | 0.0941 | 9.34 | 0.17 | 1.49 |

¹ THIS JOURNAL, 34, 735 (1912); 35, 210, 601, 616, 1897 (1913); 36, 1047, 1904 (1914); 37, 217 (1915).

The loss in weight due to drying did not decrease the activity, but an almost equal loss in weight due to heat decreased the activity 50%. Similar results were obtained with castor beans except that with them almost the whole of the activity was lost in heating.

Series of experiments were made in which the activity of both soy bean preparations was tested in solutions containing salts and alcohols of different concentrations. In each test 25 cc. of solution and 0.2 g. of preparation were used. The action on ethyl butyrate in water alone is small, so that practically no effect was noticeable due to added substance in most cases. Only in 0.1 *N* sodium fluoride and in the most concentrated sodium chloride solutions were marked retardations observed. Table II shows the results obtained with triacetin in salt solutions of the indicated concentrations.

TABLE II.—ACTIVITY OF SOY BEAN LIPASE PREPARATION TOWARD TRIACETIN IN VARIOUS SOLUTIONS.

| | S.B. I. | S.B. II. | | S.B. I. | S.B. II. |
|--|---------|----------|--|---------|----------|
| H ₂ O | 2.70 | 2.87 | 0.01 <i>M</i> MgSO ₄ | 3.22 | |
| 0.01 <i>M</i> NaCl | 2.98 | | 0.02 | 3.17 | |
| 0.02 | 3.08 | | 0.05 | 3.11 | 3.17 |
| 0.05 | 3.28 | 3.44 | 0.1 | 2.65 | |
| 0.1 | 3.31 | 3.52 | 0.002 <i>M</i> MnSO ₄ | 3.13 | 3.46 |
| 0.2 | 2.90 | 3.20 | 0.05 <i>M</i> CH ₃ OH | 2.76 | 2.61 |
| 0.5 | 2.44 | | 0.1 | | 2.53 |
| 1.0 | 1.79 | 2.53 | 0.2 | 2.54 | 2.78 |
| 0.05 <i>M</i> NaBr | 3.37 | | 0.5 | 2.65 | 2.40 |
| 0.1 | 3.46 | 3.60 | 1.0 | 2.29 | |
| 0.2 | 3.11 | 3.38 | 0.01 <i>M</i> C ₂ H ₅ OH | | 2.74 |
| 0.5 | 1.95 | | 0.02 | | 2.52 |
| 0.1 <i>M</i> NaI | 2.46 | 3.16 | 0.05 | 2.53 | 2.49 |
| 0.1 <i>M</i> NaF | 0.40 | 0.34 | 0.1 | 2.51 | 2.57 |
| 0.1 <i>M</i> Na ₂ SO ₄ | | 2.23 | 0.2 | 2.54 | 2.52 |
| 0.2 | | 1.95 | 0.5 | 2.26 | 2.31 |
| 0.5 | | 1.39 | 1.0 | 1.90 | |

The S.B. II preparation showed a greater activity than did the S.B. I preparation in almost every case. With sodium chloride, the activity increased with increase in concentration of the salt until the concentration 0.1 *N* was reached, and then decreased with more salt. With sodium bromide, a similar maximum activity was observed at 0.1 *N*. Sodium fluoride exerted a very marked retardation. Magnesium sulfate accelerated in dilute (0.01 *M* to 0.05 *M*), and retarded in more concentrated solution. Manganous sulfate accelerated strongly. Methyl alcohol and ethyl alcohol exerted no appreciable effect in dilute solutions (up to about 0.1–0.2 *M*); at greater concentrations, retardation was observed. This was greater with ethyl alcohol than with methyl alcohol. On the whole, these lipase actions towards triacetin in solutions of different substances resemble very closely those previously reported with the

castor bean and duodenal lipases, so that similarities in their chemical nature may fairly be deduced from the similarities in their chemical behavior under various conditions.

Some extraction experiments were made with S.B. I.¹ 0.2 g. of preparation was treated with 25 cc. water for the lengths of time indicated, filtered through asbestos with suction, the activities of the filtrates tested and the residues either extracted again or tested for lipolytic action. The results are given in Table III.

TABLE III.—ACTION OF AQUEOUS EXTRACTS OF SOY BEAN PREPARATION (S.B. I) ON (a) ETHYL BUTYRATE AND (b) TRIACETIN (24-HOUR TESTS).

| | Filtrate. | Residue (H ₂ O). ² | Total. |
|---|-----------|--|--------|
| (a) Direct tests, not filtered.....0.45 | | | |
| One minute extraction..... | 0.13 | 0.31 | 0.44 |
| 24 hrs. extraction..... | 0.17 | 0.15 | 0.32 |
| Second successive 24 hrs. extraction..... | 0.02 | 0.17 | 0.36 |
| (b) Direct tests, not filtered.....2.70 | | | |
| One minute extraction..... | 1.07 | 1.29 | 2.36 |
| 24 hrs. extraction..... | 1.45 | 0.93 | 2.38 |
| Second successive 24 hrs. extraction..... | 0.24 | 0.87 | 2.56 |

The fractional parts of the two types of activity extracted by water did not differ much. This, taken with the preceding results, indicates that very little, if any, esterase (active toward ethyl butyrate) is present in the soy beans, but that considerable quantities of lipase (active toward triacetin) are. The amounts of the latter which were extracted by water ranged from 45% for the one minute extractions to 66% for two successive 24 hrs. extractions. These results differ markedly from the results obtained with castor bean preparations, which showed two types of action which could be separated by their different solubilities.

The filtrates obtained in these extractions were somewhat cloudy as a rule. On dialyzing these for 24 hrs. in collodion bags against running water, the cloudiness was increased with the separation of small amounts of precipitate. These dialyzed solutions on repeated filtration through hardened filters gave perfectly clear solutions which showed very nearly the same activity toward triacetin as the original undialyzed extracts. The solubility of the lipase of soy beans to form a clear solution in water is in marked contrast to the properties of the castor bean enzymes. There the esterase was found to be soluble and the lipase insoluble in water. The addition of three volumes acetone to the soy bean lipase solution precipitated a light gray powder, which, after grinding with fresh acetone and drying in a vacuum desiccator showed no activity, and on analysis gave a nitrogen content (Kjeldahl) of 14.0%.

¹ Cf. IX Paper, THIS JOURNAL, 35, 1904 (1913), for similar experiments with the castor bean lipase preparation.

² Residue treated with 25 cc. water and the activity tested.

A number of extraction experiments were made with sodium chloride solutions of different concentrations. In these, 0.5 g. S.B. II were extracted with 60 cc. solution for 24 hrs. at room temperature, filtered through asbestos, the filtrates dialyzed for 20 hrs. in collodion bags against running water, and then tested for 24 hrs. The results were corrected for purposes of comparison to show the activities obtained from 25 cc. of original undialyzed extract. Toward ethyl butyrate practically no activity was shown by the extracts. Toward triacetin the following mean results were obtained:

| | | | | | | | | |
|-----------------------------|------|-------|-------|-------|-------|-------|-------|-----------|
| Conc. NaCl solution..... | 0 | 0.5 M | 1.0 M | 1.5 M | 2.0 M | 2.5 M | 3.0 M | Saturated |
| Activity found (Triac.).... | 1.13 | 1.48 | 1.52 | 2.11 | 1.10 | 1.06 | 1.07 | 0.59 |

A marked maximum is observable for the 1.5 M solution; that is to say, this solution extracted most active lipase, almost twice as much as water. The behavior of these salt solutions toward soy beans is strikingly similar to their behavior toward castor beans.¹ In both cases, the maximum quantity of lipase is extracted by 1.5 M sodium chloride solution (about 9% solution). This concentration of salt solution is also very near that generally used in extracting proteins from seeds.² The residues from extracting the soy beans with the different salt solutions on a second extraction and filtration with salt solutions of the same strength as before, showed very little activity in the filtrates.

Some analyses of the S.B. II preparation may be of interest. The methods used were the same as those previously described. The substance, dried in a vacuum desiccator over phosphorus pentoxide, showed a nitrogen content of 8.9%, ash 4.46%, P₂O₅ 1.41%, CaO 0.31%, and MgO 0.66%. The forms of combination of the nitrogen in the preparation, according to Van Slyke's method, were the following, expressed as percentages of the total nitrogen: Ammonia, 10.6; melanine, 4.3; arginine, 16.0; cystine, 3.7; histidine, 5.7; lysine, 6.5; amino nitrogen in filtrate, 47.1; non-amino nitrogen in filtrate, 3.3; total, 97.2%. The preparation gave strong tests for tyrosine (Folin reagent) and for carbohydrates (Molisch test).

The writer wishes to thank Mr. K. Sugiura for his aid, especially in making the analyses, and Mr. M. Erenstoff for his help in much of the experimental work.

Summary.

The lipolytic properties of soy beans were studied by the methods used in the similar studies of castor beans and of duodenal contents.

A comparison of some of the properties of these hydrolytic enzymes showed the following relations:

Soy beans contain a lipase active toward triacetin (and therefore presumably toward fats), somewhat soluble in water, with a maximum solubility in 1.5 N sodium chloride solution. Castor beans contain an esterase soluble in water and a lipase insoluble in water and soluble in sodium

¹ XII Paper of this series, *THIS JOURNAL*, 37, 217 (1915).

² Cf. Osborne, "The Vegetable Proteins," 1909, p. 16.

chloride solution with a maximum solubility at the concentration 1.5 *N*. Duodenal contents contain an esterase and a lipase, the former predominating in the intestinal juice, the latter in the pancreatic juice and bile.

Marked similarities in the action of neutral salts and alcohols are shown by the lipases from different sources.

The action of heat and of drying on the soy bean lipase was found to be similar to their action on castor bean lipase and esterase.

The analyses of the soy bean lipase preparations showed no marked differences in comparison with the analyses of the castor bean preparations.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE BIOCHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

ENZYMES OF THE CENTRAL NERVOUS SYSTEM.

By H. M. ENGLISH AND C. G. MACARTHUR.

Received January 13, 1915.

The enzymes of the brain and nerves have not been investigated as thoroughly as those of most other tissues. This is rather surprising when one considers the supreme importance of the nervous system. Most of the previous data on brain enzymes has been obtained as part of other investigations, the enzymes of the nervous system having been considered only incidentally. The work here presented had for its object the beginning of a more systematic study of the enzymes of nervous tissue and a somewhat more detailed study of the most important ones.

Preparation of Extracts.

For the larger part of this work fresh sheep brains, packed in ice soon after removal from the animals and expressed directly from Chicago, were used. The membranes and blood vessels were removed and the brain divided into cerebrum, cerebellum, medulla, mid-brain, and, in some cases, corpus callosum. These divisions were minced separately in a meat grinder, then ground to a fine state in a mortar, with either toluol or oil of mustard as a preservative, usually the latter, and extracted with water 0.2% HCl, 0.9% NaCl, 0.5% Na₂CO₃, chloroform water or glycerin. In each case 1 cc. of the liquid was used for each gram of brain tissue.

As a check on this method and also for the sake of comparison with other methods the following procedures were carried out:

The ground tissue (with or without preservative) was spread in thin layers on watch glasses and placed in large desiccators. The glasses were surrounded by a cylindrical screen outside of which calcium chloride was placed. The desiccator was placed in a jar and packed with ice and salt. When the tissue was frozen the desiccator was evacuated. By frequent renewing of the vacuum the tissue could be dried in one to two days. A part of this dried material was tested directly while the rest was ex-

tracted twice with benzene by continual shaking in a mechanical shaker. After this treatment a light powdery substance was left. When this was used for enzyme study an amount of extractive and water was used that so compared with that used on the moist tissue that the enzyme content should be comparable.

The chief objection to this ideal method is that it cannot easily be used on large amounts of material and it is somewhat slow. A quicker method is to spread the ground tissue and preservative in very thin layers on glass plates. These plates were placed in a specially constructed box through which a current of air was drawn by an electric fan. By frequent turning, the tissue can be dried in ten to fifteen hours. Some of this air-dried material was treated with benzene to remove the lipoids, as had been done with the tissue dried by the freezing method.

In making the extractions the tissue was placed in cheesecloth sacks and suspended in wide mouth bottles containing the extractives. More preservative was added and the bottles stoppered. These were usually left at room temperature for from three to seven days. The sacks were then lifted out of the extractives, allowed to drain for a few hours and discarded. The extracts were placed in a refrigerator and used as soon as possible.

The test solutions were ordinarily prepared as follows: 4 cc. of substrate were added to 10 cc. of extract and 100 cc. of water. The solution was mixed thoroughly and exactly 50 cc. placed in each of two 150 cc. flasks. One of these was boiled to destroy the enzymes, and both were then placed for 48 hrs. in an air thermostat kept at 37.5°. When a large number of tests were to be run on the same substrate, a solution was made containing the right proportions of substrate and water and 100 cc. of this solution used for 10 cc. of extract. In the case of insoluble substrates like olive oil and ethyl butyrate, emulsions of these were produced by making the liquids slightly alkaline and thoroughly shaking. When activators were used they were always added to the enzymes before the substrate had been put in.¹ After 48 hrs. in the thermostat the amount of activity was determined. For the action on fats, fat-like compounds and salol, direct titration was made with 0.1 *N* sodium hydroxide using phenolphthalein as indicator. For the action on proteins the formaldehyde method was used. With amylases the amount of activity was estimated by the copper hydroxide reduction test.

Results and Discussion. 1. Lipase.

Extractives for Lipase.—It was desirous at the outset to find the best method of extracting the enzymes, or at least a good method. It is obvious that the method which might prove best for one enzyme might be

¹ Rosenheim and Shaw-Mackenzie, *J. Physiol.*, 40, Pro. VIII (1910).

a very poor method for extracting others. Active lipolytic extracts¹ were obtained with all the solvents used.

Two such series after extracting for seven days gave the following results when acting on a mixture of equal amounts of monoacetin and monobutyryl:

TABLE I.

| Tissue. | Extractive. | 0.1 N NaOH required for neutralization. | |
|--|--------------------------------------|---|------|
| | | Cc. | Cc. |
| Fresh cerebrum..... | H ₂ O | 1.34 | 0.85 |
| Fresh cerebrum..... | 0.2% HCl | 0.13 | 0.24 |
| Fresh cerebrum..... | 0.9% NaCl | 1.21 | 0.82 |
| Fresh cerebrum..... | 0.5% Na ₂ CO ₃ | 1.30 | 0.70 |
| Fresh cerebrum..... | CHCl ₃ water | 1.34 | 1.13 |
| Fresh cerebrum..... | Glycerin | (3.75) ² | 0.78 |
| Frozen cerebrum, no preservative.... | H ₂ O | 1.94 | .. |
| Frozen cerebrum, no preservative.... | Glycerin | (0.11) | .. |
| Frozen cerebrum with preservative.... | H ₂ O | 2.31 | .. |
| Air dried cerebrum..... | H ₂ O | 1.37 | .. |
| Air dried cerebrum (ext. with benzene) | H ₂ O | 2.71 | .. |

Another series of extractions was run on the cerebrum with a view of finding out the rate of extraction of the various liquids. In this series ethyl butyrate was used as a substrate.

TABLE II.

| Tissue. | Extractive. | 0.1 N NaOH required for neutralization after extracting for | | | |
|---------------|--------------------------------------|---|----------------|----------------|-----------------|
| | | 5 days. Cc. | 7 days. Cc. | 9 days. Cc. | 12 days. Cc. |
| Cerebrum..... | H ₂ O | 0.30 | 1.25 | 1.18 | 1.83 |
| Cerebrum..... | 0.2% HCl | 0.19 | (0.85) | 0.50 | 0.57 |
| Cerebrum..... | 0.9% NaCl | 0.38 | 0.60 | 1.10 | 1.19 |
| Cerebrum..... | 0.5% Na ₂ CO ₃ | 0.45 | 0.64 | 1.30 | 1.18 |
| Cerebrum..... | Glycerin | 0.15 | 0.14 | 0.37 | 0.50 |

The results of these experiments indicate that water, sodium chloride, sodium carbonate and chloroform water are about equal as extractives. The acid extractive seems to be less well suited for extracting the lipase, since the values for its activity are considerably lower. Probably the difference in the results with the various extracts of glycerin is due partly to the substrate used and partly to the amount of water present with the glycerin. It will be noticed that with the frozen dried tissue the amount of activity, when extracted with glycerin (no water being present), was

¹ J. H. Coriat, *Am. J. Physiol.*, **12**, 353 (1904); A. Pagenstecher, *Biochem. Z.*, **18**, 285 (1909); A. Wroblewski, *Compt. rend.*, **152**, 1334 (1911); L. Buetow, *Biochem. Z.*, **54**, 40 (1913).

² The values in parenthesis are not considered comparable and are obviously inconsistent with the other data given. Explanations for these apparent discrepancies will be given wherever possible.

very small. The value 0.78 agrees best with other data on the glycerin water extracts and is very likely the most reliable one for comparison.

The drying method in general seems to give slightly better results than the direct extraction method. The air-dried tissue extracted immediately with water gave about the same activity as the fresh tissue extracted with water, the figures being 1.34 and 1.37. The air-dried tissue which had been extracted with benzene gave the highest activity of any of the dried portions. Just why this is true is not clear, unless the lipoids exert an inhibiting or protecting influence upon the lipase.

With the frozen tissue extracted with water greater activity was obtained than with fresh tissue extracts. The tissue frozen without a preservative gave a little less activity than that in which a preservative was used. (A preservative was used in both cases when the extractions were made.) It is doubtful if these figures are of any great significance other than the fact that the preservative, which was oil of mustard in these series of experiments, exerted no inhibiting influence upon the enzyme.

Best Medium for Lipase.—With regard to the nature of the medium in which the lipase acts best, experiments show that a medium of slight acidity is best suited to its activity. In testing out this point, alkaline extracts were used in two different experiments. In one flask the solution was left alkaline, while in the other a slight acidity was produced. Similarly acid extracts were tried out in both acid and alkaline media. With a mixture of monoacetin and monobutylin, the following results were obtained:

TABLE III.

| | Cc. 0.1 N NaOH. | |
|---|-----------------|------|
| | I. | II. |
| 0.5% Na_2CO_3 extract; slightly acid..... | 1.15 | 0.70 |
| 0.5% Na_2CO_3 extract; slightly alkaline..... | 0.79 | 0.37 |
| 0.2% HCl extract; slightly acid..... | 0.33 | 0.24 |
| 0.2% HCl extract; slightly alkaline..... | 0.17 | 0.18 |

The alkaline extract as shown before is more active than the acid, but larger activity is produced by the alkaline extract if the medium is made slightly acid at the start. The acid extract likewise is better suited to an acid medium.

Substrates.—The lipase found in different portions of the brain possesses the power of acting on many substrates. Some results obtained with different extracts are given in Table IV.

There is no basis for comparison of the various extracts of this table since the conditions under which the different experiments were carried on were varied.

The best substrates are triacetin and monoacetin. Tributyrin, monobutylin and ethyl butyrate were acted upon quite readily. Lard, tallow

and butter may owe their lesser activity to the fact that they do not go into solution and at best form only finely divided particles when ground with water in a mortar or thoroughly shaken with water. Cephalin and lecithin were affected to the same degree as olive oil. No specificity of action was noticed with brain lipase other than the one of rate of hydrolysis of the various substrates.

TABLE IV.

Cc. of 0.1 N NaOH required for neutralization.

| Substrate. | Water ext. of cerebrum. | | | Na ₂ CO ₃ ext. of cerebrum. |
|---------------------|-------------------------|------------------------|------------------------|---|
| | Water ext. of cerebrum. | Water ext. of medulla. | Water ext. of medulla. | |
| Triacetin..... | .. | .. | 0.56 | 0.36 |
| Monoacetin..... | 1.37 | 2.80 | .. | 0.29 |
| Tributylin..... | .. | .. | .. | 0.24 |
| Monobutylin..... | 0.84 | 2.40 | 0.25 | 0.08 |
| Ethyl butyrate..... | .. | 2.23 | 0.15 | 0.13 |
| Olive oil..... | 0.15 | 0.26 | 0.29 | (0.56) |
| Lard (hog)..... | .. | .. | .. | 0.19 |
| Tallow (beef)..... | .. | .. | .. | 0.16 |
| Butter..... | .. | .. | .. | 0.17 |
| Lecithin..... | 0.25 | 0.19 | .. | .. |
| Cephalin..... | 0.20 | 0.27 | .. | 0.23 |

Conditions Best Suited for Action.—Since the activity at any one time depends upon a large number of conditions it was decided to run a set of experiments in which each condition in succession would be varied while the others would be constant. The different conditions varied were the amount of extract, the amount of substrate, the substance used as an activator, the amount of dilution, and the time during which the enzyme was allowed to act. The substrate used was ethyl butyrate.

In preparing the solutions in these experiments, a considerable amount of each proportion of ethyl butyrate and water desired was made slightly alkaline and thoroughly emulsified. When used, the emulsion was thoroughly mixed with the extract and two equal amounts of the mixture taken, one for a check and the other for enzyme activity. In the cases where an activator was used, it was always mixed with the extract before either was added to the substrate.¹ The figures in the results represent the cc. of 0.1 N NaOH required to neutralize the difference between the check and normal flasks.

Where one set of conditions was varied the remaining conditions were kept under circumstances found favorable in previous experiments. Thus, when the amount of extract was varied with the amount of substrate, no activator was used, the dilution was 50 cc. and the time two days. When the amount of dilution was varied with the time, 5 cc. of extract were used, 0.2 cc. of substrate, and no activator.

The results indicate clearly that the amount of activity of the brain

¹ Rosenheim and Shaw-Makenzie, *J. Physiol.*, 40, Pro. VIII (1910).

TABLE V.
Activators.

| | Cc. | Substrate in cc. | | | NaH ₂ PO ₄ NaHPO ₄ | Sodium Glyco- cholate. | Sapenin. | Dilution in cc. | | | Time in days. | | |
|---|-----|------------------|------|------|--|------------------------------|----------|-----------------|--------|------|---------------|------|--------|
| | | 0.1. | 0.2. | 1. | | | | 0. | 25. | 100. | 1. | 3. | 6. |
| Extract..... | 2 | 0.19 | 0.28 | 0.41 | 0.22 | 0.12 | 0.20 | 0.28 | 0.09 | 0.10 | 0.07 | 0.31 | 0.60 |
| | 5 | 0.26 | 0.37 | 0.53 | 0.38 | 0.31 | 0.34 | 0.49 | 0.36 | 0.44 | 0.18 | 1.40 | 1.65 |
| | 15 | 0.40 | 0.64 | 1.25 | 0.55 | 0.20 | 0.60 | (1.60) | 0.44 | 0.68 | 0.28 | 1.60 | 2.15 |
| Substrate..... | 0.1 | | | | 0.20 | 0 0 | 0.15 | 0.40 | 0.30 | 0.27 | 0.10 | 0.47 | 0.68 |
| | 0.2 | | | | 0.30 | 0.41 | 0.34 | 0.53 | 0.44 | 0.49 | 0.19 | 0.52 | 1.03 |
| | 1.0 | | | | 0.92 | 0.53 | 0.68 | 0.77 | (1.30) | 0.53 | 0.61 | 0.88 | 1.43 |
| Activators. { Na ₂ HPO ₄ } NaH ₂ PO ₄ } Sodium } Glycocholate } Sapenin..... | | | | | | | | (1.80) | 0.57 | 0.60 | 0.25 | 0.58 | 1.25 |
| | | | | | | | | 0.22 | 0.12 | 0.34 | 0.14 | 0.48 | 0.65 |
| | | | | | | | | 0.35 | 0.34 | 0.50 | 0.22 | 0.63 | 0.97 |
| Dilution..... | 0 | | | | | | | | | | 0.30 | 0.70 | (0.68) |
| | 25 | | | | | | | | | | 0.18 | 0.45 | 1.05 |
| | 100 | | | | | | | | | | 0.23 | 0.84 | 1.29 |

lipase on ethyl butyrate varies directly with the amount of enzyme, and the amount of substrate, used. In every case with the exception of one, the activity was increased where either one of these factors was enlarged. The one exception is the case of the variation of the amount of extract with sodium glycocholate as an activator. Here the greatest activity, contrary to expectations, was obtained in the flask containing 5 cc. of extract and not in the one containing 15 cc.

In varying the dilution a peculiar result was obtained. Activity was, as a rule, greater in both the smallest and largest dilutions than it was in the medium dilution. This may be accounted for by supposing that water inhibits the enzyme, but that the larger the dilution the oftener the interacting molecules collide.

In the flasks in which the time of action of the enzyme was varied, the amount of activity gradually increased with the time. With one exception, there was no evidence of the end point having been reached even at the conclusion of the sixth day.

With the activators the results were less definite. The amount of phosphates used was 2.5 cc. of a 1% solution of equal amounts of the mono-basic and dibasic phosphates of sodium. 2.5 cc. of a 0.02 molar solution of sodium glycocholate, and 2.5 cc. of a 0.25% solution of saponin were used. The greatest activity was obtained with the phosphates and the least with the sodium glycocholate, although the activity was not increased markedly in any case. As is to be noticed from the table, it is doubtful if the activity was increased at all with sodium glycocholate. If any conclusion can be drawn it would seem to be that sodium glycocholate does not markedly increase the activity of brain lipase on ethyl butyrate under any of the conditions under which it was tested.

With saponin slightly higher activity was obtained, but this was not much above the normal activity. The three values obtained for saponin when the amount of extract was varied, were 0.20, 0.34, and 0.60. The three corresponding normal values were 0.28, 0.37, and 0.64. When the amount of substrate was varied, the three values were 0.15, 0.34, and 0.68, while the normal values were 0.26, 0.37, and 0.53. It would seem from these latter results that saponin has more influence in larger amounts of substrate, although the differences are not sufficient to guarantee this conclusion. The values obtained for the activity of saponin under different dilutions do not differ to any appreciable extent from the normal values. With the different lengths of time the values are also close to normal.

The values obtained with a mixture of mono- and dibasic phosphates acting on different amounts of enzyme are approximately equal to the normal values, and the amounts of activity obtained with the two smaller concentrations of substrate are not far from the normal values, but the value obtained with phosphates acting on a large amount of substrate is

considerably higher than the corresponding normal value, the figures being 0.92 and 0.53, respectively. This result would seem to indicate that phosphates, like saponin, increase the activity in large concentrations of the substrate. The results obtained for different lengths of time through which the enzyme was allowed to act are not markedly different from the values obtained when no phosphates were present.

In regard to the influence of activators on the action of the enzyme, it should be stated that larger increases in activity were obtained when monoacetin was used as a substrate with a water extract of the cerebrum. Values obtained under comparable conditions are as follows:

TABLE VI.

| | Cc. 0.1 N NaOH. |
|--|-----------------|
| 5 cc. ext., 0.2 cc. monoacetin..... | 2.87 |
| 5 cc. ext., 0.2 cc. monoacetin, 2.5 cc. 0.02 <i>M</i> sodium glycocholate..... | 3.05 |
| 5 cc. ext., 0.2 cc. monoacetin, 2.5 cc. 0.25% saponin sol. ¹ | 3.11 |
| 5 cc. ext., 0.2 cc. monoacetin, 2.5 cc. 1.0% phosphate sol. ² | 3.63 |

From these results it will be seen that sodium glycocholate and saponin slightly increased the activity of the lipase, while phosphates increase it markedly. Previous investigators¹ have shown that saponin and sodium glycocholate considerably increase the activity of the pancreatic lipase. The accelerating action of phosphates on the brain lipase has also been reported.²

Lipase in the Different Divisions of the Brain.—The different divisions of the brain when kept under conditions as nearly as possible identical and extracted with water, gave the following activity:

TABLE VII.

| | Cc. of 0.1 N NaOH. | | | Cc. of 0.1 N NaOH. | |
|-----------------|--------------------|------|----------------------|--------------------|------|
| | I. | II. | | I. | II. |
| Cerebrum..... | 1.34 | 1.25 | Medulla..... | 0.45 | 0.36 |
| Cerebellum..... | (2.10) | 0.87 | Corpus callosum..... | 0.61 | 0.56 |
| Mid-brain..... | 1.25 | 1.23 | | | |

These results indicate clearly that the gray matter is more active from a lipolytic standpoint than the white. The corpus callosum which is made up almost entirely of white matter would naturally be expected to give the lowest activity, but although it was obtained as free as possible from gray matter, it nevertheless showed greater activity than the medulla. The activities of the two cerebrums were about equal, while the activity of one cerebellum was higher and the other lower than those of the cerebrum and mid-brain. Very probably the lower value is nearly correct. Since the mid-brain contains large nuclei of gray matter, it seems probable that the greater part of its activity depends upon these. The medulla,

¹ Rosenheim and Shaw-Mackenzie, *J. Physiol.*, 40, Pro. VIII (1910).

² A. Wroblewski, *Compt. rend.*, 152, 1334 (1911).

which is very similar to the mid-brain structurally but lacks the large nuclei, showed considerably less activity.

Lipase in Brains of Different Animals.—Human, beef, sheep, and dog brains have been tested for lipolytic activity and all found to be active. No experiments were run with extracts from each source under strictly comparable conditions, so that an exact estimate could not be made of the relative quantities of lipase contained in the brain from the different sources. Figures which were obtained from extracts of the different brains acting on triacetin are given below:

TABLE VIII.

| | Cc. 0.1 N NaOH. | | Cc. 0.1 N NaOH. |
|---------------------|-----------------|---------------------|-----------------|
| Human cerebrum..... | 3.50 | Sheep cerebrum..... | 4.31 |
| Beef cerebrum..... | 4.50 | Dog cerebrum..... | 3.60 |

While these values do not give an accurate idea of the lipase content of the different brains, they nevertheless show that all have the ability to split triacetin to about the same extent.

2. Proteolytic Enzymes.

The presence of a proteolytic enzyme¹ in nerve tissue has been indicated by the action of tissue extracts on various proteins. Time did not permit of an extensive study of this enzyme, or enzymes; but it has been found to attack several different proteins. A glycerin-water extract of the cerebrum prepared by the freezing method gave the following results when the resulting solution was tested for amino acids by the formaldehyde method:²

TABLE IX.

| | Cc. 0.1 N Ba(OH) ₂ . | | Cc. 0.1 N Ba(OH) ₂ . |
|------------------|---------------------------------|----------------------|---------------------------------|
| Egg albumen..... | 0.2 | Witte's peptone..... | 0.95 |
| Gelatin..... | 1.92 | Nuclein..... | 0.69 |
| Casein..... | 0.98 | | |

The splitting of Witte's peptone was expected because of the presence of erepsin in most of the tissues so far studied; but it would seem that erepsin alone would hardly account for the large action on the more complex proteins, and it is probable that a pepsin or trypsin-like enzyme, or both, are present throughout the brain as well as in the hypophysis where both have been found.³

The proteolytic action of brain extracts on Witte's peptone takes place most rapidly in alkaline medium.

TABLE X.

| | |
|--|------------------------------------|
| Witte's peptone, slightly acid medium..... | 0.50 cc. 0.1 N Ba(OH) ₂ |
| Witte's peptone, slightly alkaline medium..... | 1.92 cc. 0.1 N Ba(OH) ₂ |

¹ Kutscher and Lohman, *Z. physiol. Chem.*, **39**, 313 (1903); H. M. Vernon, *J. Physiol.*, **32**, 33 (1904); A. Wroblewski, *Compt. rend.*, **152**, 1334 (1911); L. Buetow, *Biochem. Z.*, **54**, 40 (1913).

² S. P. L. Sorensen, *Biochem. Z.*, **7**, 45 (1908).

³ L. Buetow, *Biochem. Z.*, **54**, 40 (1913).

Tests of the various kinds of extracts on Witte's peptone gave the following amounts of activity, 5 cc. of extract and 5 cc. of a saturated solution of peptone being used in each case:

TABLE XI.

| | 0.1 N Ba(OH) ₂ . | | 0.1 N Ba(OH) ₂ . |
|----------------|-----------------------------|---|-----------------------------|
| Water..... | 0.15 | 0.5% Na ₂ CO ₃ | 0.25 |
| 0.2% HCl..... | 0.12 | CHCl ₃ H ₂ O..... | 0.21 |
| 0.9% NaCl..... | 0.16 | C ₂ H ₅ (OH) ₃ | 0.45 |

Here again the acid extract is shown to form a poor medium for the action of the protease. The sodium carbonate extract is better, but the highest activity was obtained with the glycerin extract and the results of a previous table show further that that extract was effective on other proteins as well as on Witte's peptone (Table IX).

3. Other Brain Enzymes.

In searching for *rennin*, negative readings were obtained by the use of the metacasein test.

The *amylase* content of brain tissue seems to be very slight.¹ No action at all could be detected in tests on starch, glycogen, amygdalin, sucrose, maltose, lactose, and dextrose. Dextrin, however, was slightly hydrolyzed. A solution of *dextrin* in which the enzyme had been allowed to act, gave a slight copper hydroxide test for the presence of a reducing sugar, while the check solution gave no test. The glucosides, arbutin and salol² are hydrolyzed by water extracts of the brain. A solution of *arbutin* after being acted upon by the enzyme gave a strong copper hydroxide test, while in the boiled check no copper was reduced.

With *salol* the following results were obtained by direct titration of the solutions:

TABLE XII.

| | Cc. 0.1 N NaOH. |
|---|-----------------|
| Unboiled flask containing enzyme and salol..... | 1.52 |
| Boiled flask containing enzyme and salol..... | 0.76 |
| Difference = enzyme activity..... | 0.76 |

Since the cerebroside, cerebrin, contains a galactose grouping, it was thought possible that this might be split off by the amylase, but in several tests made on a mixture of cerebroside no reduction of copper was obtained.

Catalase can easily be proved present in brain tissue. A water extract of the cerebrum was divided into two portions, one of which was boiled. Equal amounts of these two solutions were then mixed with equal amounts

¹ A. Wroblewski, *Compt. rend.*, **152**, 1334 (1911); Wohlgemuth and Szecsi, *Z. Neurol. Psych.*, **13**, 454 (1913); L. Buetow, *Biochem. Z.*, **54**, 40 (1913); V. Kafka, *Zentr. Biochem. Biophys.*, **14**, 294 (1913).

² A. Wroblewski, *Compt. rend.*, **152**, 1334 (1911).

of hydrogen peroxide, placed in fermentation tubes and set in the thermostat. At the end of two hours the tube containing unboiled solution had in it from four to eight cc. of gas which proved to be oxygen, while the boiled check had produced no gas. The results show that the decomposition of hydrogen peroxide, which takes place at a slow rate under normal conditions, is greatly accelerated by the presence of the brain extract, and since such acceleration is not produced by boiled extract, it must be due to some thermolabile compound contained in the extract.

Tests were made for other enzymes and negative results obtained.

*Peroxidase*¹ was tested for by the guaiac test, in which guaiac, in the presence of hydrogen peroxide, is turned blue if the enzyme is present. No blue coloration was obtained. Tests for *oxidase* also resulted in the negative. A solution of alpha naphthol was not changed to a blue color in the presence of a tissue extract as is the case when certain oxidases are present;² formaldehyde was not oxidized to formic acid; and xanthin and hypoxanthin were not converted into uric acid. It is probable, since both of these enzymes have been reported by several investigators, that conditions were not exactly favorable for their detection or the specific tests were not used. It has been shown that glucose³ and other powerful reducing substances, haemoglobin,⁴ and protein interfere with different oxidase tests.

Reductase could not be demonstrated by the methylene-blue test which depends upon the decoloration of a dilute solution of methylene blue by formaldehyde. Here again the conditions may have been unfavorable for the action of the enzyme.

Guanase, which transforms guanine into xanthine, and *urease*,⁵ which produces carbon dioxide and water from urea, could not be detected in the brain extracts. It is probable that both of these, if present at all, are present in such small quantities as to be undetectable by the methods used.

Summary.

1. The brain contains a lipase, erepsin, an amylase, a catalase, enzymes which decompose arbutin and salol, and probably a pepsin or trypsin-like enzyme, or both.
2. The lipase and proteases are best extracted by a mixture of glycerin and water or by water.
3. Extracts of tissue, dried either by the freezing or air-current method, showed greater activity than extracts of fresh tissue.
4. The highest activity was obtained from tissue extracted after drying with benzene to remove the lipoids.

¹ Levene and Stookey, *Biochem. Z.*, 13, 44 (1903).

² F. Traetta-Mosea, *Gazz. chim. ital.*, 43, II, 138 (1913).

³ E. Sieburg, *Z. physiol. Chem.*, 86, 503 (1913).

⁴ Czyhlarz and v. Furth, *Hofmeister's Beitr.*, 10, 358 (1907).

⁵ L. Buetow, *Biochem. Z.*, 54, 40 (1913).

5. Triacetin and monoacetin form the best substrates for the action of the lipase. Lecithin and cephalin are also acted upon by it.

6. The amount of activity of the lipase, as has been shown for other enzymes, is increased directly with the amount of enzyme, the amount of substrate, and the time during which the enzyme is allowed to act.

7. The amount of activity of the lipase is increased by the presence of sodium glycocholate, saponin, or a mixture of the mono- and dibasic phosphates of sodium.

8. The lipase acts best in a slightly acid medium, the erepsin in an alkaline medium.

9. In general, the gray matter is more active than the white. Higher activity was obtained with extracts of the cerebrum, cerebellum, or mid-brain than with extracts of the medulla, or corpus callosum.

10. Human, beef, sheep, and dog brains all contain similar amounts of lipase.

11. Negative results were obtained in tests for peroxidase, oxidase, reductase, guanase, urease, and rennin.

URBANA, ILL.

NOTE.

The Origin of Petroleum.—It has been some time since I suspended publication on various lines of study on petroleum and its constituents, and it therefore seems necessary, to retain this field, that a brief mention be made of the present condition of my work, that others may not with perfect propriety take up some parts of it which I now have in progress. I am now using the information gained during the last thirty years in aid of further examination of the constituents of petroleum with especial reference to their original formation. It appears that twenty or more crude oils including those of Russia, South America, Texas, Canada and Louisiana contain the identical series of nitrogen compounds that were formerly described as present in California petroleum. These compounds are not pyridine as was formerly made plain in the paper on the California oils. This subject I have now in hand, together with a method for the determination of the small proportions of nitrogen contained in crude oils.

I am also carrying on a study of the action of sulfur on the constituents of petroleum, the series C_nH_{2n+2} , C_nH_{2n} , C_nH_{2n-2} , and C_nH_{2n-4} . Hydrogen is readily removed at temperatures near 150° with the formation of heavier oils, and at the same time with the formation of sulfur derivatives of the hydrocarbons. It is proposed to include in these changes the hydrocarbons all the way to the asphalts. I also have in hand series of hydrocarbons obtained by the distillation of coal *in vacuo*, and of gilsonite

in vacuo; the latter yields about 50% of its weight in distillates. These have been fractioned *in vacuo* and await further examination.

CHARLES F. MABERY.

CASE SCHOOL OF APPLIED SCIENCE,
CLEVELAND, O.,
January 28, 1915.

NEW BOOKS.

Essays and Addresses. By the late JAMES CAMPBELL BROWN, D.Sc. (Lond.), LL.D. (Abdn.), Professor of Chemistry in the University of Liverpool. With a portrait and twenty-two illustrations. J. & A. Churchill: London, 1914. vii + 208 pp. Price, \$2.00 net.

This book has been published in response to the request of many of the former pupils and friends of Dr. Campbell Brown for copies of addresses, either never published, or at present out of print. Five of the twelve numbers were delivered before the student chemical society of the University College, Liverpool, and two others before a joint meeting of the societies of the same college, while three were delivered before the Liverpool Section of the Society of Chemical Industry, two of them being addresses as Chairman of the Section.

Perhaps the most interesting papers are the translation of an autobiographical sketch of Liebig, originally published in the *Deutsche Rundschau*, and a reminiscent sketch of Hofmann. Speaking of the long hours kept by students, assistants, and Hofmann himself, in the little group at the Royal College of Chemistry, he adds: "That is the kind of work that tells. An eight-hour day may be all very well for working men who have no ambition and who are content with daily bread (and beer); but a gentleman has to work much harder." Other essays on technical education and chemistry as a profession, discuss perennial problems in an interesting manner, while the papers on Ethics of Chemical Manufacture, and a French View of German Industries, are far from being out of date. The only strictly scientific paper is one on Aquiculture: a Study of Deposits in Pipes.

The book as a whole is pleasant reading, and will be especially welcome to the old students and many friends of the genial Liverpool professor.

JAS. LEWIS HOWE.

Zur Lehre von den Zuständen der Materie. By P. P. VON WEIMARN. Vol. I, 183 pp. Vol. II, 100 photographic illustrations. Theodor Steinkopff, Dresden & Leipzig. Price M. 7 unbound, M. 9 bound.

This is a reproduction of the author's articles in the *Kolloid Zeitschrift*, 1908-9, without much of the theoretical matter then published.

Proceeding on the idea that every insoluble substance is capable of assuming the colloidal state by sufficient subdivision, he devotes much of the experimental work to the forms of barium sulfate. This and

aluminum hydroxide are the basis of a thorough study of the conditions of matter in the colloidal solution and solute states, and the author has carried his studies very far beyond the work of others on the general subject. His photographs show barium sulfate as perfectly colloidal, resembling gelatin, and also in all stages of crystalline growth. He supports the theory that there are no really amorphous substances and that every substance may be made to assume either amorphous or crystalline states at will.

To produce the amorphous colloidal state, the substance must be produced under conditions of very low solubility.

He ascribes to the substance a coefficient of form of precipitate (N). This determining factor he places proportional to the concentration of the four compounds in equilibrium in the metathesis which produced it, and to the quantity of the precipitating substance which must ultimately separate from the solution in granular phase, inversely proportional to the solubility of this compound and proportional to the viscosity of the solution. That is, the coefficient is the product of these factors.

The two volumes contain much interesting work. The second is devoted entirely to microphotographs. The experimental work is largely original and the whole forms an interesting suggestive addition to the more specific subject of colloids rather than to the title, "Zustand der Materie."

W. R. WHITNEY.

Handbuch der Arbeitsmethoden in der anorganischen Chemie. Edited by DR. ARTHUR STÄHLER, Privatdozent in the University of Berlin. Vol. III, first half. Veit & Company, Leipzig, 1913. 682 pages, 354 fig. Price, bound, 25 marks.

Vol. I, published in 1912, 786 pages, 1064 fig., bound 28 marks, treated of the laboratory and its equipment—mechanical operations. Vol. II, not yet published, is to be devoted to physical and chemical processes. Vols. IV and V will treat of descriptive inorganic chemistry. Volume III, of which this is the first half, is devoted to physico-chemical measurements. The topics treated in this part with their authors are as follows: Vapor Density, Osmotic Pressure, Viscosity, Diffusion, Conduction of Heat and Specific Heat (Eucken); Weight, Volume and Density (Fellgentraeger); Surface Tension (Freundlich); Density of Gases (Guye); Metallurgy (Gerens and Ruer); Compressibility and Thermal Expansion (Heuse); Solubility of Gases (Just); Critical Constants (Klemensiewicz); Boiling and Subliming Points (Krafft); Compressibility and Thermostats (Richards); Molecular Weights in Solution (Sieverts); Calorimetry and Heat of Reaction (Steinwehr); Solubility and Adsorption (Thiel); Melting Points (v. Wartenberg).

As this list indicates the plan of the entire work involves the coöperation of a brilliant corps of co-editors, including in addition to those whose names occur above, many well-known chemists, each writing on one or more subjects in which, as a rule, he himself has been an active investiga-

tor. In some chapters, as for example, that on weighing, matters of real interest to the specialist are preceded by a detailed discussion of the most elementary topics. In other chapters, notably that dealing with the determination of molecular weights by the boiling point method, long descriptions of primitive forms of apparatus are given, the inclusion of which might be the subject of criticism were it not for the fact that the latest improved forms are also described, thus giving the reader the history of the evolution of the subject.

The result is the production of an exhaustive as well as an authoritative treatise that must become indispensable to all advanced workers in the field of general and physical chemistry. HERBERT N. MCCOY.

The Elements of Physical Chemistry. By J. LIVINGSTON R. MORGAN, PH.D., Professor of Physical Chemistry in Columbia University. Fifth edition. New York: John Wiley and Sons. Small octavo, pp. xiv + 506. Cloth, \$3.00 net.

This book now appears in a fifth edition, and its general arrangement and Ostwaldian heredity are doubtless already familiar to those interested. The author remarks that, in this edition, the discussions of the phase rule and of the subject of colloidal solutions have been restricted, because special works on these subjects are now available. The system of notation employed has been changed throughout in order to conform to that adopted by the International Commission for the Unification of Physico-Chemical Symbols. The 238 problems comprised under Chapter X will still be found useful, in spite of the works of Prideaux and of Knox. The commendable effort to keep the book modern is perhaps more successful in individual detail than in general viewpoint. It is with regret that one finds that such errata have escaped notice as appear on p. 389: "The unit of electrical resistance is the *ohm*. . . . This is equal to 10^9 ergs. The unit of current strength. . . . is called the *ampere*—equal to 10^{-1} ergs. The unit of electromotive force is the *volt*, or 10^8 ergs." Truly, as Bret Harte would say, it were better for the student to know fewer facts clearly than more facts in a confused way. ALAN W. C. MENZIES.

Handbuch der Mineralchemie. DOBLTER, *et al.* Vol. II, No. 6 (Bogen 1–10) and Vol. III, No. 5 (Bogen 41–50). Theodor Steinkopff: Dresden and Leipzig. Price, M. 6.50 each.

The editors of this work are to be congratulated that the European war has not lessened their output up to the present time, though the name of one of them, Dittrich, who has heretofore contributed the analytical methods, is conspicuously absent from this latest issue.

The contents of Vol. III, No. 5, is devoted chiefly to the mineral arsenates. They are mostly rare and have been the subject of little chemical work. There are only about a dozen references to work done in the last decade and a comparison of what there is about them with the matter

of a first-class mineralogy (Dana's) shows only slight additions. The subject of antimony is begun in this heft.

Vol. II, No. 6, deals with the important aluminum silicates. The anhydrous natural silicates are satisfactorily treated and the matter on porcelain is definite and adequate. The clay minerals, especially kaolin, possess great interest to the geologist and have been the subject of literally hundreds of investigations. Much of this work appears to be mere rubbish and its treatment in *Mineralchemie* seems to the abstractor open to serious criticism; page after page of futile experimentation is recorded in detail where a paragraph or two with references would have been all the matter is worth. This situation has occurred rather frequently in *Mineralchemie*, and while the effort of the editors to deal with all data in an unprejudiced manner is to be commended, definiteness and unity have often been inexcusably sacrificed.

E. T. ALLEN.

A Laboratory Manual of Qualitative Analysis for Students of Medicine, Dentistry and Pharmacy. By A. R. BLISS, JR., Professor of Chemistry and Pharmacy in the Birmingham Medical College. W. B. Saunders Company: Philadelphia, 1914. Octavo of 244 pages with 8 tables. Cloth, \$2.00 net.

This small book is even smaller than it appears, about one-third of the pages being blank to receive the notes of the student. Nevertheless the ground covered seems to the writer to be adequate to the needs of students of Dentistry and Pharmacy and of prospective students of Medicine. For medical students the book should be used during one of the preliminary college years, for there is certainly no time for this work in the better medical schools. In order to meet the increasing demands for preliminary training in chemistry before entering the medical school, *Qualitative Analysis* should, in the writer's opinion, encroach upon the laboratory time of the first course in college chemistry and be given in the second half of the freshman year. Only in this way can sufficient training in Organic Chemistry and Quantitative Analysis be obtained in the two years of college work now required for entrance to most of the good medical schools. In such a scheme this manual would be very serviceable, for it contains under each element, in addition to the usual qualitative reactions and plan of separation, a list of common compounds and especially of the "official" pharmacopoeial preparations.

An extensive knowledge of many of the latter preparations is perhaps of doubtful value to the physician, who has so many more important and more useful chemical facts and principles to learn, but the names and composition of the "official" compounds should at least be brought to the student's attention, and the inclusion of the list for consideration during the work in *Qualitative Analysis* seems to the reviewer desirable.

For students of pharmacy and dentistry and for students in those medical schools which still find it necessary to give *Qualitative Analysis*

as a part of the medical course, this book should also prove acceptable.

P. A. SHAFFER.

Traité Complet d'Analyse Chimique appliquée aux essais industriels par J. Post et B. Neumann, avec la collaboration de nombreux chimistes et spécialistes. Deuxième édition française entièrement refondue, traduite d'après la troisième édition allemande et augmentée de nombreuses additions par G. Chenu et M. Pellet. Tome troisième, second fascicle. Paris: Librairie Scientifique, A. Hermann et Fils. 1913. 465-902 pp. Price, 15 francs.

In this fascicle, itself a book of 438 pages, two related subjects are discussed: Coal Tar, and Coloring Materials. The general treatment is the same as in other fascicles, already reviewed in *THIS JOURNAL*,¹ and the same standard of excellence is maintained. Here again, however, as in the first instalment of this volume, the space does not seem to be equitably divided between the topics. It cannot be reasonably objected that 403 pages is too much to devote to pigments and to coal-tar dyes and their raw materials, vegetable dyes, dyeing and chemical tests. Coal tar is disposed of in 35 pages, but perhaps the excuse for this lies in the fact that both sections were written by G. Schultz, of Munich, so that any deficiency in one place can be remedied in another. C. E. W.

Der Nachweis organischer Verbindungen. Ausgewählte Reaktionen und Verfahren. VON L. ROSENTHALER, Professor an der Universität Bern. Die chemische Analyse. Sammlung von Einzeldarstellungen auf dem Gebiete der chemischen Analyse. Band XIX/XX. Stuttgart: Ferdinand Enke, 1914. Large 8, 1070 pp. Price, 34 Marks, unbound; 32.30 Marks, cloth.

The author explains in the preface that his aim has been to assemble upon a sufficient theoretical foundation the material facts of organic qualitative analysis which seemed to be of the most importance to the practicing analyst, after having verified and supplemented them, so far as possible, by his own observations. The result is probably the most comprehensive collection of analytical characterizations of organic compounds of all classes that has been brought within the compass of a single volume.

No rigid general scheme of procedure is laid down; but after a few sensible words of advice on the principles which will usually guide the analyst in planning his examination of unknown compounds or mixtures, and a section on the qualitative determination of the elements in organic compounds, the main portion of the book is given up to a series of descriptions of the analytically important reactions and properties of approximately three thousand compounds. The value of these characterizations is enhanced by the occasional discussion of methods for particular separations and extractions, and abundant bibliographical references. At the beginning of each chapter the analytical reactions of greatest importance for the class of compounds contained in it, and particularly such as are useful for

¹ *THIS JOURNAL*, 31, 120 (1909); 34, 752 (1912).

establishing the membership of individuals in the special groups, are clearly presented, and their uses indicated.

The grouping of the subject matter may be best indicated by naming the chapter titles. These are: Hydrocarbons; Alcohols; Aldehydes; Ketones; Carbohydrates; Phenols; Acids; Oxyacids; Ethers; Quinones; Esters; Halogen-derivatives; Nitro-derivatives; Nitroso-derivatives; Nitriles; Acid-amides; Amines; Acid-derivatives of Bases; Heterocyclic Bases; Amino-acids; Sulfur Compounds; Arsenic Compounds; Alkaloids; Resin Acids; Tannins; Glucosides; Bitter Compounds; Dyestuffs; Proteins; Enzymes; Toxalbumins.

A table of the compounds described, placed at the end of the book and arranged according to the elements present and the melting and boiling points, tends to lessen the difficulties arising from the lack of closer analytical coördination between the class reactions.

The author has done his work with care and discrimination, and the resulting volume, which is attractive in appearance, will prove a valuable book of reference.

S. P. MULLIKEN.

Applied and Economic Botany. By HENRY KRAEMER. Especially adapted for the use of students in technical schools, agricultural, pharmaceutical and medical colleges, and also as a book of reference for chemists, food analysts and students engaged in the morphological and physiological study of plants. 8°. Pp. vi + 806, with 424 plates comprising about 2,000 figures. Philadelphia, published by the author (145 N. Tenth St.), 1914. Price, \$5.00.

Two addresses, respectively by the President of the Botanical Society of America and the Chairman of the botanical section of the American Association for the Advancement of Science, at the recent Convocation Week meetings in Philadelphia, present the very different viewpoints from which botany, like the other sciences, must be seen by those to whom the privileges and duties of teaching fall. The practical utilization of every one of the fundamental sciences has become so great that the teacher can hardly make peace with his conscience if he lets his one opportunity, with students who take an introductory course only, go by with little or no reference to its applications, while those to whom the arts based upon it and other sciences are of more direct interest than the science itself are impatient of the use of their time and effort for more of the latter than they see or believe to be of practical use. This is true of the sciences directly fundamental to engineering, agriculture, and the like, for instance, to such an extent that in the former, to which physics is indispensable, its teaching has become so specialized that in a great university with a strong college of engineering, the general student who has escaped physics in the secondary school may have difficulty in finding opportunity in college to learn the salient facts and relations in physics that every intelligent person needs; while a civil engineer who is to know the distinguishing

marks of structural timber, or the sanitary engineer who is to recognize the danger line in the bacterial contents of drinking water, must acquire the desired knowledge with little or no understanding of the structure and life of plants which forms the essence of an intelligent comprehension of our every-day dependence upon these humble relatives of mankind.

Professor Kraemer is a seasoned teacher in the field of pharmacognosy, in which, almost to our day, a general knowledge of botany has been considered indispensable, and which, even now, he and those of his training and practice are unwilling to reduce to an art divorced from the underlying science. The present book is doubly interesting as a concrete exposition of this viewpoint and a compendium of reference for the botanical facts most frequently desired by pharmacists and organic chemists, to whom the source and origin of their materials are important. It is the outgrowth of long experience in the laboratory, and may be regarded as the most mature expression of the author's views, since it replaces earlier books from his pen in the same field. Dealing primarily with the structure and products of plants, it is necessarily lacking in the full analysis of their activities that the agriculturist is coming more and more to recognize as fundamental to agronomy—though physiology is by no means excluded from its pages; but a student who had really mastered its contents in the laboratory would form excellent material for the development of a specialist in any field of botany, if he had absorbed at the same time the spirit of investigation that its intelligent use ought to foster.

Little need be said in detail of the contents of the book, further than that it is modern and accurate as these attributes may be applied to a compendious work of its kind. An outline of the vegetable kingdom occupies about one-fifth of its space, with a chapter on organic evolution. Somewhat more concerns the contents and forms of cells, and a like part is given to the external and internal structure of plants. Chapters on botanical nomenclature and terminology and on the cultivation of medicinal plants give a reference character as valuable as it is unusual in books usually accessible to those who are neither botanists nor pharmacists; a far too short chapter presents the essentials of technique as practiced by the student of drugs; and over one-third of its bulk consists in a synopsis, at once readable and instructive, of the vegetable kingdom and its products. Not the least of its merits is that the book is fully indexed.

WILLIAM TRELEASE.

Chemistry of Common Things. By RAYMOND P. BROWNLEE, ROBERT W. FULLER, WILLIAM J. HANCOCK AND JESSE E. WHITSIT. Allyn and Bacon: Boston, New York and Chicago. 1914. viii + 616 pages. Price, \$1.50.

The authors of this book are teachers in high schools of New York City, and their work is an attempt to satisfy a practical requirement in public school teaching by furnishing a manual which "is designed to meet the

growing demand that high school courses should 'prepare the pupil for citizenship;" it therefore deals with the chemistry of everyday affairs.

The authors have shown great industry in bringing together a large number of facts relating to applied chemistry. The compilation might almost be described as an elementary chemical technology and if a student is interested at all in the things which go on around him he should find much in this book that is entertaining and probably helpful.

There is no attempt at a presentation of the principles of chemistry in a systematic way and not much is given in the nature of general chemical theory. The course is not intended for "discipline," but to impart information to that large class of young people who never expect to go to college. Such information must be of necessity somewhat superficial, but, all things considered, it is perhaps the wisest plan. Teachers are divided on this point. The reviewer believes that the greatest mistakes are made in trying to follow a rigorously scientific method with beginning students; it sometimes happens that at the end of the freshman year the boy has neither facts nor discipline, and after a high school course the situation may be, if possible, even worse.

The present book contains, however, too much material for high school purposes and the authors admit that only portions of it can be used. It shows frequent evidences of hasty preparation, calling for not a few corrections in future editions. For example, the equations on pages 9 and 10 illustrating the action of iodine on mercury and of oxygen on phosphorus should be changed. In one of the early chapters boric acid is described among the important acids. The erroneous statement is made that it and its salts are largely employed as food preservatives. In the attempt to give some information on an unusually wide range of topics this information is frequently incorrect as well as superficial. An example of this is shown in the discussion of alcoholic beverages on pages 218 and 219. The water analysis quoted on page 169 would doubtless prove somewhat confusing to a beginner. But these and other faults may be easily corrected in future editions.

J. H. LONG.

Lehrbuch der physikalischen Chemie. By JELLINEK. Ferdinand Enke, Stuttgart, 1914. Vol. I, 732 pp. Unbound, 24 marks; bound, 34 marks.

This is the first volume of a treatise on physical chemistry, which the author intends to carry out in the characteristic Teutonic spirit of exhaustive research. We may hope that the present war will not prevent its ultimate accomplishment.

The completeness of the author's scope is indicated by the fact that the 732 pages in the present volume suffice merely for the consideration of the fundamental laws of chemistry and thermodynamics and for the consideration of matter in the gaseous and liquid states.

The author's treatment is largely conventional, as it should be in a work which is to serve as a compendium of existing knowledge. The general method of treating any particular field of investigation is to discuss in turn the experimental methods, the experimental results and their theoretical interpretation. Without being offensively elementary the presentation is pedagogical in the best sense, thus permitting the use of the book by chemists not previously familiar with the particular field treated. The complete references to the literature will prove of special value.

The author's presentation of the principles of thermodynamics seems very clear and satisfactory. He defines free energy in the familiar Helmholtz form which makes the decrease in free energy equal to the maximum obtainable external work instead of the maximum work minus the imposed work, which is the definition more often used in chemical calculations. Let us hope that he will stick to his own definition more consistently than is the custom of German chemists.

The author has very wisely postponed the presentation of the Nernst heat theorem until a later portion of his work. In spite of the fact that valuable principles are certainly connected with the Nernst theorem and that considerable progress in the way of systematic presentation has been made by Planck in the third edition of his *Thermodynamics*, it seems to the reviewer that the exact definition and significance of the principle is still a problem for the future. The reviewer hardly believes that it will be possible, as Jellinek apparently intends, in his later treatment, to identify the Nernst heat theorem with the principle stating the impossibility of attaining the absolute zero of temperature, since this principle is one which has long been familiar to thermodynamic thought.

The specific heat of gases is treated from the standpoint of the simple Einstein quantum theory, which to the reviewer certainly seems less unsatisfactory than any of the more complicated quantum theories, all of which are in a rather unsatisfactory stage of development.

The book, if brought to completion, will certainly rank as a standard treatise on physical chemistry, and will perform a valuable service for which Ostwald's *Allgemeine Chemie* becomes less adequate as the science of physical chemistry advances. Even with only one volume published it is a valuable contribution to systematic knowledge and might well find a place in every library of physical chemical books.

RICHARD C. TOLMAN.

Die Wasserstoffionenkonzentration. By PROFESSOR DR. LEONOR MICHAELIS, Privatdozent an der Universität Berlin. Julius Springer, Berlin, 1914. xiii + 210 pp. Price, M. 8.

This book is the first volume of a series of "Monographien aus dem Gesamtgebiet der Physiologie der Pflanzen und der Tiere," and its purpose

is primarily to show the absolute necessity of considering the hydrogen ion concentration in biological processes, and to explain clearly how it can be measured.

The author considers, first, the theoretical meaning of the "hydrogen number," *i. e.*, the logarithm, with the minus sign omitted, of the hydrogen ion concentration. This division includes discussions of the dissociation of water, acids, bases and amphoteric electrolytes, the hydrolysis of salts, the influence of the hydrogen ion concentration on the coagulation of colloids, and its influence upon the action of the most important ferments.

The second division gives experimental results on the hydrogen ion concentration in various fluids of the living organism.

The third main division of the book describes the theory and technique of the measurement of the "hydrogen number" by means of the hydrogen electrode and by means of indicators. There is included also a discussion of the preparation of solutions of definite hydrogen number.

There has been a great need for just such a book as this, and the author has succeeded in filling it admirably. In books which seek to place the methods or results of one branch of science at the disposal of another, one often finds a superficial knowledge of one field or the other, but the author of the present work writes neither as a physical chemist assuming the role of prophet to the biologists, nor yet like a biologist who has acquired a smattering of physical chemistry. The book should, therefore, prove of great value not only to biologists but also to many of the chemists who need the information that it gives.

JOEL H. HILDEBRAND.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal
(Founded by Ira Remsen)

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE COMPLICATIONS AT THE ANODE IN THE SILVER COULOMETER (VOLTAMETER).

By T. W. RICHARDS AND F. O. ANDEREGG.

Received February 13, 1915.

In a recent paper we have emphasized anew one of the important causes of error in the silver coulometer, namely, inclusion of mother liquor in the precipitate.¹ A definite decision concerning this matter necessarily preceded the discussion of all other questions involving the weight of the cathode deposit, on account of the fact that included matter may seriously affect this weight. A brief repetition of the main conditions is perhaps in order.

(1) It was shown that the amounts of inclusion are highly variable, being dependent upon extent of surface covered by the cathode deposit and the roughness of surface of the cathode, as well as upon the presence of some kinds of impurities. The rate of deposit is doubtless also of moment; and yet other circumstances may affect the outcome.

(2) When the solution is very pure, the extent of surface limited and the surface smooth, the amount of inclusion may be very small (as little as 0.004%), but it is not safe to rely upon its constancy, unless very unusual precautions are observed. With reasonable but not excessive precautions

¹ Richards and Anderegg, *THIS JOURNAL*, 37, 7 (1915).

the amount may be seven or eight times as great, even when using materials much purer than these ordinarily obtainable.

(3) Although the amounts of inclusion may thus be quite different under different conditions, sufficiently accurate results may be obtained if the volatile portion of the enclosed mother liquor is expelled by heating the deposit to dull redness. Therefore, this should always be done, applying the correction mentioned in paragraph (5) below.

(4) Part of the included mother liquor is enclosed between the crystals and the dish, and part entirely within the silver crystals.¹ The proportions thus distributed doubtless vary with the conditions. Of the former part, a portion may be evaporated at 160°, but probably not all of it.² For this reason satisfactory quantitative results concerning the amount of the inclusion may not be obtained from the crystals after scraping them from the dish; for some water is probably evaporated, and some silver nitrate is certainly left on the dish, when the intervening cells are opened by the abrasion.

(5) In the most accurate work correction should be made for the residual silver left by the decomposition of the enclosed mother liquor. As the amount thus left is very small, it is not necessary to know the exact concentration of the liquid; an approximation will suffice.³

(6) *The really essential point is to determine the true weight of pure silver deposited by the current from a sufficiently pure solution.*

(7) All these conclusions essentially confirm and amplify the Harvard

¹ Hulett and Vinal have found in some recent interesting experiments (*Bull. Bur. Stand.*, 11, 553 (1914)) that silver in contact with platinum is perceptibly soluble in water. That this solubility was too small to affect the question under consideration is shown by the fact that our crucibles with the adhering silver, after thorough washing, could be allowed to stand for many hours filled with pure water without imparting enough silver to that water to show in the nephelometer. Accordingly, the silver nitrate which we found upon the scraped crystals and upon the battered electrode from which they had been removed, must have been really the result of included mother liquor. Upon our other comparative results the solubility of silver in water would have no effect as all samples were treated in practically the same way.

² The cells are evidently, some of them, opened by the high steam pressure at 160°, the crystals having been loosened by the difference between the coefficients of expansion of silver and platinum. Water imprisoned wholly within the silver walls of cells in detached crystals requires, as has been repeatedly stated, a dull red heat for its liberation.

³ It is clear that the evaporation of part of the included mother liquor complicates estimation of the amount of silver nitrate included, but, fortunately, the possible error is very small. The resulting surplus of silver nitrate is partly balanced by the fact that the enclosed catholyte must have been somewhat depleted. Therefore, for ordinary cases it is safe to conclude that the residual silver must weigh about 6% or 8% of the total inclusion from a 10% solution. Of course, for work of the very highest accuracy (beyond 1 part in 100,000) the exact nature of the inclusions must be determined and a more complete method must be used.

results of 1902.¹ We believe that they are also in essential accord with the heretofore published results of Hulett, making allowance for certain differences of detail already mentioned.

Before our further experiments are recounted, a few words about the history of the question may not be out of place, although a detailed discussion of the very voluminous literature would occupy too much space for the present publication.

In the early work at Harvard it had been shown that the older form of voltameter, containing filter paper as originally designed, invariably caused a deposit distinctly heavier than that in which the anode liquid is kept away from the cathode.² At least part of this effect was referred to a temporary surcharge of silver in the anolyte. The need of a substantial inorganic septum to separate this liquid being indicated, a porous cup was employed, and the use of filter paper entirely abandoned. More recently Rosa and his collaborators have concluded, on the basis of extended experiments, that part of the effect is due to a specific action of filter paper and not to the surcharge of silver.³

There has been much discussion of these conclusions, but unanimity of opinion does not seem to have been attained.⁴ A study of the published experiments seems to indicate that both of the effects are probably operative at the same time; nevertheless, on account of the divergence of opinion, it seemed worth while to make further experiments concerning the nature of the anode liquid under varying circumstances. The present paper recounts the fulfilment of a portion of this program.

In studying this problem two different methods were used in the investigation to be described. In the first place, the weights of the cathode deposits in different forms of coulometers arranged in series were compared. These coulometers were so planned that the access of the anode liquid to the cathode was greatly varied, in some cases almost all of it being

¹ Richards and Heimrod, *Proc. Am. Acad.*, **37**, 415. On page 436 occur the following words: "It is evident that the amount of included mother liquor required varies according to the rate and mode of deposition;.....but in applying a correction one should obviously use the value found in the particular investigation under review."

² Richards, Collins and Heimrod, *Proc. Am. Acad.*, **35**, 144 (1899); Novak, *Proc. Roy. Bohem. Acad. Sci. Prague*, **1**, 387 (1892); Rodger and Wilson, *Phil. Trans.*, **186A**, 631 (1895); Kahle, *Z. f. Instruk.*, **17** (1897); *Ann. d. phys.*, **67**, 1 (1899); Rodger and Wilson and Kahle had all previously shown that on repeated electrolysis solutions which had been used in such an instrument gave heavier deposits than fresh solutions.

³ *Sc. Papers*, Bureau of Standards, Nos. **194**, **195**, **201**, **220**. Reprinted from *Bull. Bur. Stand.*, **9**, pp. 151, 209, 493; **10**, p. 475 (1912-1913). Many references are given in these papers, which need not be repeated here.

⁴ Smith, *Phil. Trans.*, **207A**, 545 (1908); Jaeger and von Steinwehr, *Z. f. Instruk.*, **28**, 327, 353 (1908); *Ibid.*, **33**, 321, 353 (1913); Janet, Laporte and de la Gorce, *Trav. Lab. Centr. d'Elec.*, **2**, 288, 318 (1912); von Steinwehr, *Bull. soc. Int. Elec.*, **8**, 178 (1911).

excluded, and in other cases much of it being admitted to the cathode. The various results thus obtained show that the anode liquid really contains an excess of silver, which it deposits with the normal crystalline precipitate, provided that the transfer is rapidly made.

Again, other experiments were instituted in which it was shown that silver plates immersed in fresh anode liquid, but not electrically connected, definitely gain in weight in that liquid. This outcome substantiates the other.

Comparison of Different Forms of Coulometers.

The modifications of coulometer which were compared in the experiments to be described were as follows: First, two standard coulometers, each precisely similar to that used by one of us with the assistance of G. W. Heimrod twelve years ago, were mounted. They consisted of large lipped crucibles, each weighing about 60 g. and containing about 120 cc., within which were suspended from glass arms small, porous, cylindrical Pukal cups which contained the anolyte, always at least 1 cm. in level below the catholyte.¹ One of these crucibles was employed in moderately roughened condition, caused by long using, and another was highly burished. To test the effect of size, a much larger but otherwise similar porous cup coulometer, containing over 300 cc. and having twice the surface, was used; and to test the effect of the anode liquid a very permeable cup was substituted for the fine-grained one.

These instruments were not only compared with one another, but also with the older forms. In two tests the porous cup was omitted and filter paper substituted, and in many other tests we used various modifications of the Kohlrausch form (in which neither a porous cup or filter paper are employed, but a small, glass dish is placed beneath the anode), because much use has recently been made by others of this form. The object of the glass dish, as avowed by the designers, was merely to catch the so-called "anode slime" or finely powdered deposit of silver which falls from the anode during the progress of electrolysis, since they did not fear any harmful effect from the anode liquid. In preliminary experiments we tested the original form of Kohlrausch coulometer carefully and found it unsatisfactory, partly because the "anode slime" frequently floats upon the surface of the electrolyte and becomes mixed with detached crystals from the cathode. Moreover, the cathode deposit is formed only near the top of the dish, most of the surface of the platinum cathode being useless because protected by the glass cup. This unmodified form was therefore rejected.

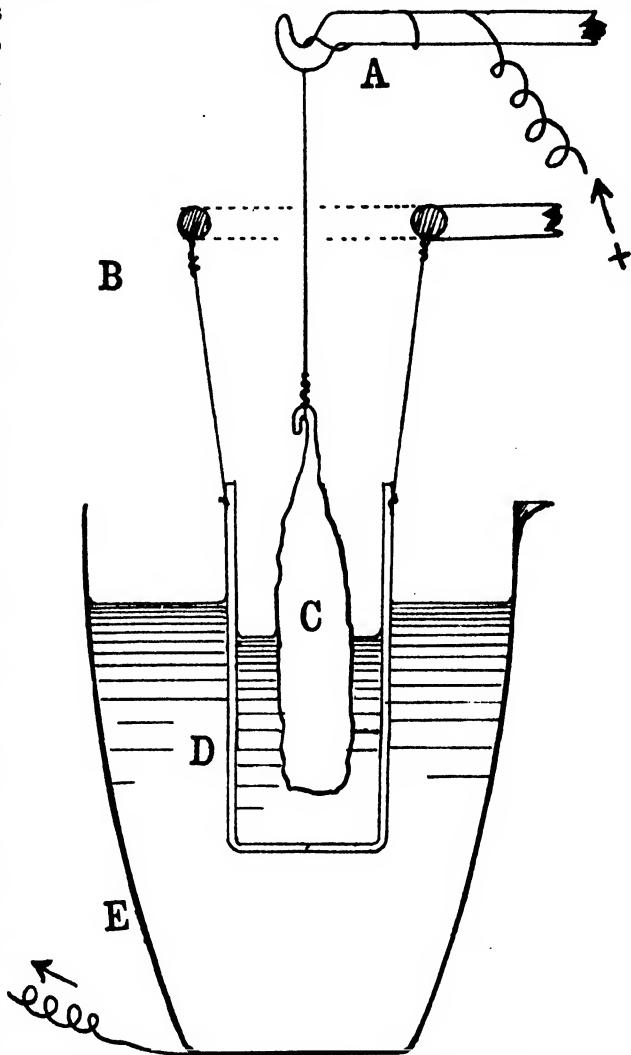
The original Kohlrausch coulometer has been modified in various ways. The form used at the Bureau of Standards had a glass ring at the surface around the anode to prevent the dissemination of the anode slime (a

¹ For further particulars, see *THIS JOURNAL*, 37, 11 (1915).

phenomenon noticed by others as well as by ourselves). Moreover, the form devised by Smith has the anode placed well down in a glass cup, and has the glass ring extended into a cylinder, which at the end of the experiment may be lowered upon the cup, thus enabling the experimenter to remove the "anode slime" and anode liquid together. This, although not different in principle, is doubtless the most easily handled modification of the Kohlrausch instrument, and is perhaps as near an approach to the porous cup as one can obtain from glass apparatus; but it is neither as convenient nor as efficient for removing the anode slime as the porous cup, and, moreover, is certainly less suitable for preventing the diffusion of the anode liquid.

In our experiments, besides the porous cup instruments, two forms of Kohlrausch coul-

ometer were finally used; first, one in which the anode was chiefly above a glass cup suspended in the electrolyte; and, secondly, one in which



Standard Porous Cup Voltmeter (actual size).

A, Glass hook for supporting anode.

B, Glass ring for supporting porous cup.

C, Silver anode.

D, Porous cup.

E, Platinum cathode (a large lipped crucible).

the anode was sunk entirely below the edges of a similar but deeper glass cup similarly suspended, the conducting wire to the anode being protected by a glass tube. In both forms the "anode slime" which accumulated at the surface was prevented from spreading by glass rings. The second of these two forms was essentially similar to that used by the Bureau of Standards under the name of Poggendorff coulometer, and is similar in principle to the Smith form, except that because our cup was deeper than theirs, it was probably a more efficient apparatus. In both these forms of Kohlrausch coulometer, the silver was deposited only on the upper half of the crucible which formed the cathode as before.

The first step in any such work is the careful testing of the standard of reference. This had indeed been carried out carefully by one of us with the help of G. W. Heimrod years ago; moreover, the consistency of results thus obtained with the help of the porous cup coulometer has been supported by various other experimenters, especially the Bureau of Standards, if we assume that the amounts of inclusion were fairly constant in experiments under similar conditions. The higher results obtained with large coulometers have already been shown in our previous paper to be doubtless due to greater inclusion of mother liquor in these cases, and, therefore, these results do not in the least militate against the results obtained with the porous cup instrument. Because of the great bulk of earlier work, but few new trials were necessary here; and these are recorded mainly in order to show that all was in order for the exact prosecution of the present research.

The following table shows results with the porous cup coulometer in which, first, a somewhat roughened cathode was compared with one very highly burnished, and, secondly, results in which the same coulometer was compared with the larger instrument, with about twice the surface and nearly three times the volume, but otherwise the same. The weights given below are those of the precipitates after ignition at incipient redness,¹ corrected for the small amount of silver (never exceeding 0.03 mg.) left by the mother liquor, which was driven off by the heat. This quantity, it may be remembered from our previous paper, was assumed to be 6% of the included mother liquor. The amount of included mother liquor was least in the small, smooth vessel; next in the small roughened vessel, and greatest in the large coulometers. The actual amounts of inclusion are given among the results tabulated in our last paper² and do not con-

¹ This measure of temperature, rather than a more exact and elaborate one, was used because it is easily available to everyone. Carefully measured, the temperature used by us was found to be between 590° and 630°. Experiments are now in progress here testing the effects of various carefully measured temperatures on the weight of precipitate.

² THIS JOURNAL, 37, 16, 20 (1915).

cern us here, for here we are concerned only with the true weight of silver deposited.

TABLE I.—COMPARISON OF POROUS CUP COULOMETERS UNDER VARYING CONDITIONS.

| | 1st Standard. Medium porous cup coulometer. Rough. | 2nd Standard. Medium porous cup coulometer. Smooth. | 3rd Standard. Large porous cup coulometer. | Errors referred to 1st standard. | |
|--------|--|---|---|-------------------------------------|---------|
| | | | | Mg. | %. |
| 1..... | 3.07914 | 3.07913 | | —0.01 | —0.0003 |
| 2..... | 3.72682 | 3.72679 | | —0.03 | —0.0008 |
| 3..... | 1.89490 | | 1.89490 | 0.00 | 0.0000 |
| 4..... | 3.13805 | | 3.13807 | +0.02 | +0.0006 |

Average error, —0.0004

Evidently, the so-called "volume-effect," which has so much troubled several investigators, has been entirely vanquished. Even considerable variations in the size and condition of the cathode make no important difference in the weight of silver obtained after ignition, all of these values being within the limit of error of experimentation. Such slight variations as exist are all in the direction indicating that the residual silver from the decomposed inclusions was slightly more than 6%—a condition which must occur if some of the cells had been opened and dried at 160°, but the error never reaches 0.001%; and as the weighings could hardly be relied upon to more nearly than 0.02 of a milligram, it is safe to conclude (as one of us concluded fifteen years ago) that the porous cup coulometer is capable after ignition of giving very constant results, and, therefore, is well suited for a definite standard of comparison.

The next step in the experimental work was obviously to repeat the comparisons, so often made by others, of the weights of silver precipitated in the other forms of coulometer with those obtained from our standard instrument, bearing in mind, nevertheless, the fact that the precipitates contained varying contamination with included mother liquor, and allowing in each case for the individual amount.

With each form of Kohlrausch coulometer a series of comparisons was made with the typical standard porous cup coulometer. In order to make the results as clear as possible and to relate them directly to the recent results of others, there is given in the first table below a comparison of the weights of the precipitates not ignited, but merely carefully washed and dried at 160°, after the manner of the several National Bureaus.

The outcome is striking. Each form of Kohlrausch coulometer is seen to give almost exactly the same results as the porous cup coulometer, just as other experimenters have found. The average result shows that in nearly 16 g. of precipitate the surplus shown by the Kohlrausch coulometer was only 0.14 mg., an error of less than one part in 100,000. It is from data of this sort that so many able experimenters have concluded

that there is no such thing as an anode impurity, that the porous cup is unnecessary, and that no inclusions are present in the cathode deposit.

TABLE II.—COMPARISON OF APPARENT WEIGHTS OF SILVER (DRIED AT 160°), DEPOSITED IN TWO FORMS OF COULOMETER.

| | No. of expt | Standard porous cup coulometer. G. | Kohlrausch coulometer. G. | Difference in weight of deposit. Mg. | Surplus in Kohlrausch forms. %. |
|---------------|-------------|---------------------------------------|------------------------------|---|------------------------------------|
| First series | 1 | 2.85028 | 2.85032 | +0.04 | +0.002 |
| | 2 | 3.07747 | 3.07746 | —0.01 | 0.000 |
| | 3 | 2.29124 | 2.29127 | +0.03 | 0.001 |
| Second series | 4 | 2.18564 | 2.18565 | +0.01 | 0.000 |
| | 5 | 3.05583 | 3.05585 | +0.02 | +0.001 |
| | 6 | 2.30750 | 2.30755 | +0.05 | +0.002 |
| | | 15.76796 | 15.76810 | +0.14 Av., | +0.001 |

Our preceding article has demonstrated, however, that the weights given in this table do not represent pure silver, but rather silver in which there is enclosed varying amounts of mother liquor in microscopic cells; hence this apparently satisfactory comparison has really little significance. The real comparison, which alone can show whether there is appreciable impurity evolved at the anode, capable of augmenting the weight of the deposit, is only to be found when the *true* weights of the silver deposited are determined by igniting the precipitates in each case, with due precautions. This had, of course, been subsequently done in each case recorded above; and Table III below presents the weights of pure silver thus found. Each of these weights is corrected for the 6 per cent. of silver assumed to be left behind by the expelled electrolyte.

TABLE III.—COMPARISON OF TRUE WEIGHTS OF PURE SILVER DEPOSITED IN TWO FORMS OF COULOMETER.

| | No. of expt. | Porous cup voltameter. G. | Kohlrausch coulometer. G. | Surplus in Kohlrausch forms. | |
|---------------|--------------|------------------------------|------------------------------|------------------------------|---------------|
| | | | | Mg. | %. |
| First series | 1 | 2.84998 | 2.85017 | +0.19 | } Av. = 0.006 |
| | 2 | 3.07714 | 3.07727 | +0.13 | |
| | 3 | 2.29095 | 2.29111 | +0.16 | |
| Second series | 4 | 2.18540 | 2.18554 | +0.14 | } Av. = 0.003 |
| | 5 | 3.05539 | 3.05548 | +0.09 | |
| | 6 | 2.30721 | 2.30727 | +0.06 | |
| | | 15.76607 | 15.77684 | +0.77 | |

Evidently in every single case the Kohlrausch coulometer gave a distinctly greater deposit of *pure* silver than the porous cup coulometer. Moreover, it is very striking that in the first series (Experiments 1, 2 and 3), where the anode was above the glass cup (giving more chance for diffusion), the surplus was much more marked than in the second series

(Experiments 4, 5 and 6), where the anode was sunk well within the glass cup. The surplus is so consistent and so much beyond the limit of error that there can be no question of its real existence.

The close agreement of the figures shown in Table II is, therefore, shown to be illusory. The reason why the porous cup and Kohlrausch voltameter appeared to give the same results was simply because in the Kohlrausch form the error of a surplus of silver from the anode was hidden by the fact that in this form the inclusions were less than in the porous cup form. The reason for the smaller amount of inclusion in the Kohlrausch form has already been shown to be due primarily to the smaller surface upon which the silver was deposited, although it may perhaps be referred partly to the different form of aggregation in larger crystals, which seems to occur when small amounts of anode liquid escape into the catholyte.¹

As has just been pointed out, the inclusions in the Kohlrausch form are less than those in the porous cup form. Evidently the amount of inclusion on the one hand and the surplus from the anode on the other hand are independent variables, and neither can be certainly predicted from a knowledge of the other.

Having thus explained the illusory agreement observed at first, and having demonstrated that a real (if slight) surplus of silver is deposited even by the best type of Kohlrausch coulometer, we may proceed to show that under conditions where the anode liquid is allowed more freely to reach the cathode, a considerably larger surplus of silver may be obtained. This indeed had been demonstrated in the early Harvard work of 1902, but much of the evidence in that work depended on a comparison of the deposit in the coulometer containing filter paper with the porous cup form, and hence some doubt might legitimately exist, as others have pointed out, whether the surplus had not been caused by the filter paper.² We shall return later to this point. It is easy, however, to promote the diffusion of the anode liquid to the cathode without introducing filter paper. All that it is necessary is to keep the liquid within the porous cup at a higher level than the liquid outside (instead of at a lower level in the manner always from the first maintained in the standard coulometer). This was done in some of the early Harvard experiments, and the result was published, although the experiments were not reported in detail and have been usually overlooked.³ Buckner and Hulett also afterwards repeated a comparison of this kind and showed that, as a matter of fact, in such cases the surplus of silver is obtained upon the cathode, using a porcelain

¹ THIS JOURNAL, 37, 16 (1915).

² Rosa and Vinal, *Bull. Bur. Stand.*, 9, 206 (1912); Laird and Hulett, *Trans. Am. Electrochem. Soc.*, 22, 345 (1912); Buckner and Hulett, *Ibid.*, 22, 381 (1912).

³ Richards and Heimrod, *Proc. Am. Acad.*, 37, 419, lines 3 to 8 (1902).

porous cup.¹ Nevertheless, it seemed worth while to repeat these experiments once more.

In the trials recorded in Table IV below, the standard porous cup coulometer was placed in series with a coulometer containing a more permeable "alundum" cup, in which the liquid was kept at a higher level inside than out, promoting diffusion as mentioned above. The "alundum" cups (which had been chosen for the purpose because they were much more permeable than the Pukal cups) were carefully tested in order to be sure that they could have no reducing action on the silver nitrate. Professor Hulett has since informed us that in some cases he had detected such action, but none was found in our samples, so that the following results are significant: The "alundum" cups (like the porcelain porous cups in all our other experiments) were not only thoroughly washed with nitric acid and water, but were also soaked in silver nitrate (as recommended by the Bureau of Standards) before being used.

TABLE IV.—INFLUENCE OF ANODE LIQUID ON WEIGHT OF CATHODE.
Dried 160°; Not ignited. Ignited.

| No. of expt. | Dried 160°; Not ignited. | | Ignited. | | Extra silver. | |
|-----------------|-------------------------------|---------------------------------|-------------------------------|---------------------------------|---------------|----------|
| | Standard coulometer. G. | Permeable alundum cup. G. | Standard coulometer. G. | Permeable alundum cup. G. | Mg. | %. |
| 7 | 2.67551 | 2.67597 | 2.67505 | 2.67539 | 0.34 | 0.012 |
| 8 | 2.41159 | 2.41208 | 2.41116 | 2.41155 | 0.39 | 0.016 |
| 9 | 2.18255 | 2.18288 | [2.18218] | [2.18241] | [0.23] | [0.010]* |
| 10 | 2.34446 | 2.34494 | [2.34406] | [2.34441] | [0.35] | [0.015]* |
| 11 | 0.94195 | 0.94217 | [0.94179] | [0.94196] | [0.17] | [0.018]* |

Average, 0.014

* Among the five trials recorded in the table, two of the electrolyses in series were conducted in the usual way, the precipitates being ignited at incipient redness as usual. The other three were conducted under the same conditions, but the weight of ignited silver was calculated from that of the silver dried at 160°, it having been obtained under the usual conditions maintained in the first two experiments. These calculated values are enclosed in brackets in the table; although not quite as certain as the more directly obtained results, they are sufficiently accurate for the purpose in hand.

The surplus of silver evident in Table III has been markedly increased in Table IV, the average in the latter series being more than double that found in the Kohlrausch coulometer where the anode was raised above the glass cup, and nearly five times that found in the form wherein the electrode was sunk within the glass cup. Probably even the "alundum" cup is not the best apparatus for demonstrating the effect of this anode liquid, for after the electrolysis is well started, the cup is partly filled with "anode slime," and the anode liquid must penetrate through this in order to escape. Because (as will be shown) the anode liquid deposits silver upon a silver surface, it must lose some of its surcharge by depositing this upon the finely divided metal of the "slime." A yet quicker removal

¹ Buckner and Hulett, *Trans. Am. Electrochem. Soc.*, 22, 379 (1912).

of the anode liquid from the neighborhood of the anode and its powdery environment would probably give a yet larger discrepancy as compared with the standard porous cup coulometer. In this connection it seems worth while to record two new experiments in which loosely wrapped filter paper took the place of the porous cup.

TABLE V.—COMPARISON OF STANDARD POROUS CUP COULOMETER WITH FILTER PAPER VOLTAMETER.

| Standard porous cup coulometer. (Ignited silver.) G. | Filter paper voltameter. (Ignited silver.) G. | Excess of silver in filter paper voltameter. | |
|---|--|---|-------|
| | | Mg. | %. |
| 2.67503 | 2.67536 | +0.33 | 0.012 |
| 2.41114 | 2.41152 | +0.38 | 0.015 |
| Average, 0.014 | | | |

There can be no question that a real excess of silver was deposited on the cathode.

Clearly, precipitates obtained in the coulometer when the anode is guarded only by filter paper are too heavy before ignition for two reasons: in the first place, mother liquor is included; in the second place, an excess of silver is precipitated. The further discussion of the action of filter paper will, however, be postponed to a subsequent paper.

Spontaneous Deposition of Silver from the Anode Liquid after Electrolysis.

In the experiments, published in 1902, made with the help of G. W. Heimrod, it was shown that the anode liquid was capable, not only of depositing an excess of silver on the cathode during electrolysis, but also of depositing silver upon a separate silver plate without any electrolytic help. In other words, it was shown that the anode liquid thus obtained had a surplus of reducible silver, which would at once crystallize on a silver surface, if it was allowed to do so before the oxygen of the air had a chance to oxidize it. Although other evidences of such behavior of the anode liquid were furnished, these results have been interpreted by others as due to the action of filter paper, and it is true that if such action existed it might account for a part of the effect, for filter paper was present. Therefore, it seemed desirable to repeat the experiment in such a way as to exclude organic matter. The problem was easily accomplished in the following fashion: The anode in a voltameter such as that used in the preceding experiments, was surrounded by a cup of easily permeable "alundum" and this in turn was surrounded by a somewhat larger, very fine-grained Pukal cup, in which the level of the electrolyte was kept below that in the inner "alundum" cell. The Pukal cup was immersed in the usual fashion in the electrolyte in the large platinum crucible-cathode, and the electrolysis was conducted as usual. During the progress

of the electrolysis, however, portions of the liquid permeating from the inner "alundum" porous cup were quickly removed by means of a fine pipet from the narrow space between the two cups, and were immediately transferred to a small porcelain crucible containing a small plate of carefully weighed silver. This plate in nine successive trials was found to gain a total of 0.62 mg., an average of 0.07 mg. in each trial. The silver plate became covered, during these trials, with a curious iridescent covering, which, when examined by a powerful microscope, was seen to consist of very fine, brilliant, crystalline laminae, probably due to the deposition of silver. But whether this was silver or something else, the essential point remains, namely, that the plate had accumulated a deposit which augmented its weight.

In order to be sure that this deposition could not be due to some impurity from the "alundum" cup, four trials were made in which precisely the same procedure was conducted, taking solutions from between the two cups, except that no current of electricity was allowed to pass. The silver showed the following gains in these successive trials: +0.01, +0.01, -0.02, +0.00 mg., total change in weight, 0.00 mg.

This indicates, not only that the weighing and method were sufficiently accurate, but also that the deposit found when the current was running could not have been due to any action of the alundum cup, but must have been due to a real addition of something (probably silver) to the liquid between the cups, and this could have come only from the anode. The result, which evidently confirms the conclusion of years ago, affords convincing direct evidence of the cause of behavior of the anode liquid observed in our other experiments. As some of the anodes in the trials just described were of fused silver, whereas others were of silver deposited electrolytically, and precisely the same average gain was noted with each class of anode, it is clear that the special form of the silver at the anode is unimportant. The production of this easily reducible surplus of silver is thus a general phenomenon.

The reason why others have failed to find this effect and, therefore, have doubted its existence, is unquestionably because they have allowed too much time or too great dilution of the anode liquid to intervene before the liquid was brought into contact with a silver surface. This would give an opportunity for oxidation, which would remove the peculiar compound causing the effect, producing a slightly basic solution capable of depositing nothing upon a silver surface, at least without electrolytic help. That a negative result is thus obtained, we have found by various experiments, which need not, however, be given in detail.

It seemed a matter of interest to discover also if filter paper alone could affect the weight of a silver plate wrapped in it and immersed in silver nitrate solution, that is to say: to discover if filter paper can produce

a silver compound capable of depositing silver in crystalline form upon a silver surface without electrolytic help. Accordingly, a silver plate was wrapped in purest quantitative filter paper, placed in a pure solution similar to that used in the regular electrolyses, and subjected to the same conditions as to length of time of standing and temperature as before. Eight successive trials showed a total gain of 0.01 mg. in the weight of the silver plate—a wholly negligible quantity. This shows that filter paper does not promptly produce in silver nitrate a compound like that produced at the anode, which is capable of depositing silver spontaneously upon a silver plate, and it removes entirely whatever doubt there may have been concerning the experiments of 1902 upon this subject.

A hypothetical explanation of the nature of the anode liquid was approved in 1902.¹ Although at the time this hypothesis was accepted only tentatively without insistence upon its final verity, no facts have been brought forward by others which seem to diminish the cogency of the argument. Therefore, it seems to us still the best explanation for the behavior of the anode solution. In brief, the hypothesis supposes that a complex ion, such as Ag_2^+ or Ag_3^+ , containing silver in a state of lower average valency than usual, is set free at the moment of the attack on the anode; that is to say: some of the silver which is properly ionized by the current carries away with it some of the anode metal, which really ought to have been left behind. This complex, not being in equilibrium with the solution, immediately decomposes,—its rate of decomposition decreasing, of course, as its concentration decreases. Most of it must decompose in the immediate neighborhood of the anode, the presence of the silver there expediting the decomposition, just as the presence of crystals of a salt relieve its supersaturation. When, however, the anode solution which contains only a slight concentration of the complex silver ion is removed from a silver surface, it is to be supposed to be more permanent, and may remain in a metastable condition until either oxidized by the dissolved oxygen in the electrolyte or precipitated upon the silver at the cathode,—which also, of course, is able to relieve the supersaturation and reduce the metastable to a stable equilibrium. Although this explanation is avowedly hypothetical, it seems to us to cover the ground and to be entirely consistent with itself and with all the facts, explaining the existence of the anode slime as well as the peculiar behavior of the anode liquid in every detail. Whether or not a portion of the anode slime, so finely divided as to be almost colloidal, may be responsible for at least a part of the phenomena

¹ *Loc. cit.*, p. 432. Novak seems to have been the first to propose this explanation (*Proc. Roy. Bohem. Acad. Sci.*, 1, 387 (1892)) and Rodgers and Watson offered independently a similar one [*Phil. Trans.*, 186A, 631 (1895)]. Reference may also be made to the work of Bose [*Z. Electrochem.*, 13, 477 (1907); 14, 85, 314 (1908)]; Luther [*Z. physik. Chem.*, 30, 628 (1900)]; Jellinek [*Ibid.*, 71, 513 (1910)], and Eisenreich [*Ibid.*, 76, 643 (1911)].

recounted in this paper, we have no means at present of deciding, but this explanation seems, on the whole, less adequate than the one just discussed. We shall hope for more light upon this question in the near future. Whatever explanation may be finally accepted, the desirability of keeping the anolyte away from the cathode by means of an effective diaphragm seems to be strongly indicated by the experiments described above.

The Nature of the "Anode Slime."

In the early Harvard papers it was suggested, as already remarked, that the hypothesis of the complex ion was capable of explaining the nature of the "anode slime." This point does not seem to have claimed the attention of others, but, nevertheless, it is worth reiterating because it is in accord with our explanation of the behavior of the anode liquid.¹ The anode dust was then found to be composed of extremely fine crystals of silver, as seen in the microscope; and we are to confirm this observation. Although it is conceivable that these crystals were left behind when a portion of the silver dissolved, it seems more probable that they are the result of the decomposition of most of the complex ion, which deposits its extra load in the form of this fine crystalline powder. With a large anode, the equilibrium at any one spot would be less difficult to maintain, hence the amount of the "slime" would be less, as the Bureau of Standards have found. That the total loss at the anode should nearly correspond to the gain at the cathode, as several investigators have shown, is not in the least contradictory to this theory, for when all the anode slime is collected and weighed with the anode, it is clear that the only weight lost must be due to such portion of the complex ion as escaped from the anode and became oxidized. In the siphon form employed, this amount would probably be very small, as the heavy anode liquid remained at the anode.² Hence, the loss at the anode and the gain at the cathode might be equal, although each might be too great. The irregular results obtained at Harvard in 1902 substantiate this explanation.³

No other theory seems to explain the existence of the anode slime and its peculiar finely divided nature as well as this.

The Efficacy of the Porous Cup as a Means of Retaining the Anode Liquid and "Anode Slime."

The above results make it perfectly clear that, in order to obtain an accurate result in the coulometer, the anode liquid must not be allowed to reach the cathode. Any device which effects this separation and permits the ready weighing of the cathode deposit should be adequate for the purpose. It is shown above that the Kohlrausch plan, which was intended originally only to collect the anode slime, serves also in part to

¹ Richards and Heimrod, *Proc. Am. Acad.*, 37, 432 (1902); *Z. physik. Chem.*, 41, 319 (1902).

² Compare *Bull. Bur. Stand.*, 10, 528, 536 (1914).

³ *Ibid.*, pp. 434 and 321, respectively.

prevent the anode liquid from reaching the cathode. But this apparatus is unsatisfactory, because even when the anode is deeply sunk within the glass cup, some excess of deposit on the cathode seems to be obtained, and in any case the anode slime is troublesome, and not always content to remain within bounds. Therefore, these forms, although better than the filter paper voltameter, do not seem to be the best.

Another device suggested by Merrill¹ places the cathode at the top and the anode at the bottom. As tested in 1902 at Harvard, it was modified by using a wire gauze as the cathode, to facilitate the escape of the depleted catholyte.² This arrangement, if the time of electrolysis is not too long and the vessel is not disturbed, secures a satisfactory exclusion of the anode liquid from the cathode; but it is hampered by the disadvantage of the possibility of the loss of small crystals from the cathode, which may fall upon the anode, and become mixed with the anode slime. It is useful when the experimenter desires that the resistance of the coulometer should remain nearly constant throughout the electrolysis.

The syphon voltameter, in which the anode and the cathode are in different vessels, has the disadvantage of interposing large resistance, which evolves heat and rapidly changes, even in the most advantageous form used by the Bureau of Standards, where the syphon is very wide and short. The reason why this has been found occasionally to give too large deposits can hardly be traced until the inclusions in such deposits have been determined. The excess is probably not due to the anode liquid, which, except in the shortest syphons, probably stays entirely on the anode side.

The elimination of these forms of coulometer leaves the porous cup coulometer as the only remaining form worthy of consideration. Therefore, it behooves us to discuss very carefully its virtues and its faults.

In the first place, it has the undeniable virtue that the anode slime on the one hand, and the precipitated cation on the other hand, are separated beyond the possibility of mixing; and the analytical determination of the weight of the cathode precipitate is certain and easy. For this reason alone it was first suggested by Poggendorff long ago; he had no inkling of the peculiar nature of the anolyte.

In the next place, the Harvard results of 1902, comparing this coulometer with other forms, (especially with the inverted wire-gauze form), seem to show indubitably that no important amounts of anode liquid escape from inside the cup into the catholyte. In order that the cup should thus be effective, it is important, of course, that there should be no large orifices in it, and that the level of the liquid within it should always be distinctly lower than that outside. Thus, if any diffusion takes place, it must be essentially from the outside inward. The cup must be very fine-grained

¹ *Phys. Rev.*, 10, 169 (1900).

² *Loc. cit.*, Richards and Heimrod, *Proc. Am. Acad.*, 37, 420 (1902).

and the absence of large holes should be tested, both by the rate of flowing from such a cup when filled with liquid and hanging in the air, as well as by causing air to be delivered through it under water. If in the latter case considerable pressure is needed, and the air escapes in a multitude of very fine bubbles from the whole surface, the cup is suitable for the purpose. If the delivery is easy, and if one point claims most of the outflow, the cup should be rejected.¹

It is, of course, possible that a trace of the offending complex ion, or whatever the compound may be which bears the surplus of silver, may be carried *electrolytically* through the cup, but there is good reason to believe from the quantitative results already quoted that this amount is so small as to be taken care of by the dissolved oxygen in the outside electrolyte before it can reach the cathode.

At any rate there can be no question that the porous cup coulometer gives very constant results. Even those who deny the necessity of its use grant this claim; and, indeed, the results of all three National Bureaus, as well as Hulett's (if we assume that under like conditions the inclusions are nearly constant), prove its constancy.

The chief objection which has been raised to the cup is the possibility that it may introduce impurities into the electrolyte. This it will do, of course, if it has not been properly cleaned. Neither an excess of acid nor an excess of alkali nor cyanide should remain in it. We believe, however, that if made of good insoluble porcelain it can cause no important impurity in the solution when it has been properly cleaned with nitric acid, thoroughly washed with water and soaked in silver nitrate solution. Moreover, it must be cleaned before every determination if an accurate result is desired. The glazing of the cup upon its upper portion, unless filling every pore, seems to be of doubtful efficacy because of the difficulty of washing out acid or other impurity which may penetrate upwards beneath the glaze.² We have found by experimental evidence that a porous cup blackened by exposure to light and dust is capable of yielding too high a deposit. In our experiments recounted above, the cups were cleaned, of course, with the greatest care, and washed until they were certainly free from acid. Ignition after such washing should not be practiced, as it alters the condition and increases the solubility of the porous silicate. Careful tests of our own—not only those described above, but also others in which the silver nitrate in cups which had been soaked were tested with permanganate—showed that our porous cups had no reducing action upon silver nitrate.

The only important difficulty which we have encountered in our own work with the porous cup is the fact that the coulometer containing such

¹ Richards and Cox, *THIS JOURNAL*, 26, 822 (1914).

² Buckner and Hulett, *loc. cit.*, pp. 371 and 380.

a cup changes its resistance somewhat as the deposit proceeds. This is more or less the case with any form of coulometer, except the inverted wire-gauze form, and in the porous cup coulometer the trouble may be minimized by keeping the levels inside and out constant by means of automatic syphons. Attention should be directed to the importance of taking the liquid from the very bottom of the anode cup, because this is where the heavy anode liquid accumulates.

Of course, nothing in this paper or the preceding paper should be construed as pretending to state the exact quantitative effect either of inclusion or of the anode liquid on any of the preceding investigations of others. So many circumstances, either already known or as yet undetermined, seem to decide the amounts of these respective effects that they can be estimated only under the special conditions present in each particular case, and cannot be exactly determined by a subsequent examination of the printed record. It may well be that some of the eminent investigators, whose work we have mentioned, have really had in their precipitates a smaller amount of inclusion, and (with the Kohlrausch instrument) a smaller anode effect than we have found in our experiments. We earnestly hope that they will determine the presence or absence of these disturbing circumstances by methods such as have been used in the present research, or by other adequate methods, so that all doubts may be removed. Especially as regards the electrochemical side of the matter this is important. Here a *constant* value for the faraday is not enough—the weights must represent the amount of pure substances chemically equivalent. The importance of this condition was seen by the Bureau of Standards as well as at Harvard in the consideration of the iodine-silver voltameter of Bates and Vinal, discussed in our previous paper.

It is to be hoped, also, that some form of precise coulometer may be found for general use, which will not involve precautions so elaborate as those recommended by some of the recent experimenters; for these are beyond the reach of many chemists and physicists. The outcome of the present research leads us to believe that results obtained by igniting the deposit in the porous cup coulometer give not only the most accurate values for electrochemical comparison, but also the safest and most easily attained standard values for the measurement of current. Perhaps when all the manifold subtle influences which determine inclusion are thoroughly known, a better way may be found; the conviction just expressed is of course based upon the actual experience up to the present time.

Because the discussion of our experiments has inevitably involved emphasis upon certain omissions in the work of other experimenters, we are especially desirous to call attention here to the real services to science rendered by them, particularly by the two series of researches

which have added most to the knowledge of the subject during the last few years.

Rosa and Vinal of the Bureau of Standards have proved, in confirmation of the early tentative Harvard results, that *under perfectly constant conditions* the porous cup coulometer, even when not ignited, gives very constant deposits. This was the main question which their careful investigation sought to answer. They have further demonstrated that certain organic impurities, including filter paper, cause striated deposits, that the contamination of the electrolyte by filter paper increases the weight of the deposit dried at 160° , that acid diminishes this weight, and that large and small unignited coulometers give lower and more nearly equal results when the electrolyte is very pure. They have presented an interesting hypothesis capable of explaining, many of these varied phenomena and exhibit excellent photographs of the striations. Although they have done little concerning the anode liquid, fortunately their lack of study of this aspect of the question has had no great practical effect on their results, because for all their chief experiments they wisely used the porous cup coulometer, in which the effect of the anode liquid is nullified.

Hulett and his collaborators at Princeton have published an interesting series of carefully obtained results, which seem to us to afford valuable support for the following outcomes of the early Harvard work: First, that the inclusions are variable under varying circumstances and often important in amount, even when the electrolyte is of a high degree of purity; and, secondly, that the anode liquid, independent of organic matter, may augment unduly the weight of the cathode. They have further made careful analyses of the chemical nature of the inclusions, showing them to consist (as had been expected) chiefly of an aqueous solution of silver nitrate. Many other matters of detail were also carefully studied by them, especially the effects caused by the presence of different gases. The recent experiments of Hulett and Vinal on the solution of silver in water, when in contact with platinum, are especially interesting.

Each of these series of investigations must be carefully studied by subsequent workers, for each contains the account of well executed experimentation concerning important aspects of the subject.

As has been already pointed out, the results and conclusions recorded in our two new papers, while in no way inconsistent with the results and conclusions just mentioned in detail, have differed in other particulars from those of these eminent investigators and of several other investigators in this field. Although there has been much private correspondence between most of those concerned during the last few months, we find no reason to alter our opinions about the main points at issue. Nevertheless, we prefer at this time to forego further discussion of these differences, especially because several of the investigators (including

one of us) are continuing their studies. The large number of variables which modify the precise working of the coulometer has led in the past to unfortunate confusion; but we hope that unanimity may before long be attained, and that the outcome of the present research may ultimately be of service in the attainment of this common point of view.

In conclusion, we wish once more to advocate strongly the use of the scientifically derived and logical name "coulometer" for this instrument, when it is used to determine accurately the number of coulombs of electricity in physical or chemical experimentation, in place of the vague and inaccurate term "voltmeter." This latter was devised before the dimensions of electrical energy were understood, and is at present an anachronism. We feel that we are second to none in the desire to do homage to the incomparable genius of Faraday; but we cannot see how the retention of this antiquated and confusing name can, in any way, enhance his credit.

We are glad to express our indebtedness to the Carnegie Institution of Washington for much of the apparatus used in this research.

Summary.

In the previous paper we have shown in verification of the early Harvard work that the inclusion of mother liquor by a silver precipitate may vary according to circumstances from 0.004 to at least 0.03% of the weight of the precipitate, and hence should be determined in each case.

In that paper we also emphasized the importance of obtaining a definite knowledge concerning the amount of imprisoned electrolyte before conclusions are drawn from the weight of the deposit.

In the present paper it is shown experimentally, confirming our earlier results and those of Hulett, that the anode liquid may really augment the weight of the ignited cathode deposit, even when no filter paper is present. This effect is presumably due to metastably dissolved silver, in the form of an argentous ion but the mechanism of the effect is not yet fully elucidated.

The Kohlrausch coulometer, although an improvement over the filter paper form, was found in our experiments not to remove all of this trouble.

An illusory agreement between different forms of coulometer was found in some of our uncorrected experiments, because of the balanced effect of the two errors (inclusion and surcharge of silver). By comparing the weights of the ignited precipitates, this compensating effect could be detected and analyzed.

The best results were produced by the use of a small porous-cup coulometer with a highly burnished cathode and pure electrolyte, the deposit being ignited at incipient redness.

These and other questions concerning the coulometer are being yet further experimentally investigated at this Laboratory.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS, URBANA, ILL., NO. 21.]

THE IONIC HYDRATION AND TRANSFERENCE NUMBERS OF CAESIUM CHLORIDE.¹

BY EDWARD W. WASHBURN AND EARL B. MILLARD.

Received January 25, 1915.

1. Outline of the Investigation.

In a previous investigation by one of the authors² the transference numbers and relative ionic hydrations of the chlorides of lithium, sodium and potassium in 1.2 *M* aqueous solution at 25° were measured by means of transference experiments in the presence of a suitable nonelectrolyte as a reference substance. The object of the present investigation was to extend these data so as to include caesium chloride, since there was much reason to believe that caesium ion is the least hydrated of all the alkali ions and there was the interesting possibility that it might be so little hydrated that the water transference would take place from cathode to anode. The previous work with sodium chloride was repeated and attempts, only partially successful, were made to include the alkali nitrates in the investigation also.

2. Purification of Materials.

Raffinose.—The raffinose was purified by recrystallization as described by Washburn and Williams,³ until a 0.1 *M* solution of the crystals had a specific conductance of less than 3×10^{-6} reciprocal ohms at 25°.

Caesium Chloride.—Part of the raw material consisted of 700 g. of polucite containing about 35% of caesium. The caesium extracted from this mineral was mixed with some caesium salts obtained from various dealers and the whole subjected to purification by recrystallization of the dichloriodide.⁴ The final product was tested with a spectroscope and found to be free from all other alkali metals except a faint trace of sodium arising from the glass vessels used as containers.

Incidentally it was found that prolonged boiling of a caesium chloride solution does not result in the volatilization of even a trace of the salt, which is contrary to a statement made by Bailey⁵ that caesium chloride is volatile with steam.

3. Apparatus and Method of Procedure.

The transference apparatus, the method of carrying out the transference experiments and the analytical methods were identical with

¹ Part of a thesis submitted by Earl Bowman Millard to the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1914.

² Washburn, *THIS JOURNAL*, **31**, 322 (1909).

³ Washburn and Williams, *THIS JOURNAL*, **35**, 751 (1913).

⁴ Wells, *Am. J. Sci.*, **43**, 17 (1892).

⁵ Bailey, *J. Chem. Soc.*, **65**, 445 (1894).

4. Notation.

| | |
|---|---|
| d_{25}^{35} | specific gravity of the solution at 25° referred to water at 4°. |
| P _r | percentage of reference substance in solution. |
| P _s | percentage of the electrolyte in the solution. |
| Ag | grams of silver deposited in the coulometers. |
| m^e | total mass in grams of electrode portion. |
| $\Delta m^w, \Delta m^w$ | increase in grams (or mols) of water in the electrode portion. |
| $\Delta m_s, \Delta n_s$ | increase in grams (or mols) of electrolyte in the electrode portion, referred to raffinose. |
| $\Delta m_s, \Delta n_s$ | increase in grams (or mols) of electrolyte in the electrode portion, referred to <i>water</i> . |
| N | equivalents of electricity passed through the solution. |
| T _c , T _e | true transference number of the cation (or anion) calculated on the assumption that the raffinose remains stationary during the passage of the current. |
| T _H ^c , T _H ^e | ordinary or Hittorf transference number. |
| Δn^w | number of mols of water transferred from anode to cathode per faraday of electricity. |
| A | anode portion. |
| M _e , M, M _c | anode middle, middle, cathode middle portions. |
| C | cathode portion. |

5. Data and Results with Sodium Chloride Reference Substance—Raffinose.

| | | | | | |
|--|---|------------------|-------------|------------------|---------|
| Composition of the solution: | | | | | |
| Sodium chloride 1.12 formula weights of NaCl per 1000 g. of water. | | | | | |
| Raffinose | 0.073 formula weights C ₁₈ H ₃₂ O ₁₆ per 1000 g. of water. | | | | |
| Applied e. m. f. | 20 volts. | | | | |
| Current | 0.10 ampere. | | | | |
| Time of run | 12 hours. | | | | |
| | A. | M _a . | M. | M _c . | C. |
| Rotation..... | 51.107° | 50.694° | 50.653° | 50.648° | 50.000° |
| d_{25}^{35} | 1.0461 | 1.0522 | 1.0522 | 1.0522 | 1.0590 |
| P _r | 3.376 | 3.331 | 3.330 | 3.330 | 3.264 |
| P _s | 5.0467 | 5.9262 | 5.9250 | 5.9263 | 6.8703 |
| Ag..... | 5.6694 | ... | ... | ... | 5.6699 |
| m^e | 120.23 | ... | ... | ... | 108.99 |
| Δm^w | —0.58 | ... | ... | ... | 0.98 |
| Δn^w | —0.032 | ... | ... | ... | 0.054 |
| Δm_s | —1.1605 | ... | ... | ... | 1.1555 |
| Δn_s | —0.01958 | ... | ... | ... | 0.01976 |
| Δn_s | —1.1221 | ... | ... | ... | 1.0915 |
| Δn_s | —0.01919 | ... | ... | ... | 0.0188 |
| N..... | 0.05255 | ... | ... | ... | 0.05255 |
| T _e = $\Delta n_s/N$ | 0.377 | ... | ... | ... | 0.376 |
| T _e | 0.623 | ... | ... | ... | 0.624 |
| T _H ^c | 0.365 | ... | ... | ... | 0.355 |
| T _H ^e | 0.635 | ... | ... | ... | 0.645 |
| $\Delta n^w/\Delta n_s$ | 1.6 | ... | ... | ... | 2.7 |
| Δn^w | 0.61 | ... | (Mean 0.82) | ... | 1.04 |

6. Data and Results with Caesium Chloride—Reference Substances

| | | Run I. | | Run I. | |
|--|------------------|--|------------------|--|---------|
| Composition of the solution: | | Composition of the solution: | | Composition of the solution: | |
| Caesium chloride 1.07 formula wts. of CsCl per 1000 g. of water. | | Caesium chloride 1.10 formula wts. of CsCl per 1000 g. of water. | | Caesium chloride 1.10 formula wts. of CsCl per 1000 g. of water. | |
| Raffinose | | Raffinose | | Raffinose | |
| Applied e. m. f. 20 volts. | | Applied e. m. f. 20 volts. | | Applied e. m. f. 20 volts. | |
| Time of run 12 hours. | | Time of run 12 hours. | | Time of run 12 hours. | |
| A. | M _a . | M. | M _c . | C. | |
| Rotation... | 48.671° | 48.225° | 48.131° | 48.116° | 47.452° |
| d ₄ ²⁰ | 1.1105 | 1.1357 | 1.1357 | 1.1357 | 1.1642 |
| P _r | 3.0320 | 2.9319 | 2.9310 | 2.8197 | 2.8197 |
| P _s | 12.077 | 14.772 | 14.770 | 14.750 | 17.713 |
| A _g | 5.5048 | ... | ... | ... | 5.5044 |
| m ^e | 132.58 | ... | ... | 119.77 | ... |
| Δm _w | —0.30 | ... | ... | 0.36 | ... |
| Δn _w | —0.166 | ... | ... | 0.020 | ... |
| Δm _s | —4.243 | ... | ... | 4.198 | ... |
| Δn _s | —0.02521 | ... | ... | 0.02495 | ... |
| Δm _s | —4.191 | ... | ... | 4.137 | ... |
| Δn _s | —0.02491 | ... | ... | 0.02459 | ... |
| N..... | 0.051027 | ... | ... | 0.051023 | ... |
| T ^c = Δn _s /N | 0.494 | ... | ... | 0.489 | ... |
| T ^e | 0.506 | ... | ... | 0.511 | ... |
| T ^c = Δn _s /N | 0.488 | ... | ... | 0.482 | ... |
| T ^e | 0.512 | ... | ... | 0.518 | ... |
| Δn _w /Δn _s ... | 0.64 | ... | ... | 0.80 | ... |
| Δn _w | 0.33 | ... | ... | (Mean 0.36) | 0.39 |
| 1 The anode residues were scorched in drying in this experiment, thus rendering uncertain the weight of the electrode portion. | | 0.45 | | 0.45 | |

those employed in the previous work and need not be described again.

The polarimeter employed for determining the concentration of the raffinose was a better and more accurate instrument than the one employed in the previous work and it was largely due to this fact that conclusive and satisfactory results were obtained with caesium chloride, the water transference being so small in amount, that a very high degree of accuracy was necessary in the polarimetric readings in order to measure its magnitude. The instrument was a triple field Schmidt and Haensch polarimeter of sufficient size to enable the use of a 100 cm. jacketed observation tube. In this tube all the solutions employed were polarized. The light was furnished by a quartz mercury vapor lamp, and was further purified by passing it through a spectroscope. The green mercury E-line was the one employed and this fact also contributed to the increase in the degree of accuracy over that obtained in the previous investigation, since the specific rotatory power of raffinose for the E-line is $[\alpha]_E = 144.55^\circ$ as against $[\alpha]_D = 123.00^\circ$ for the D-line.¹ The addition of 1.2 mol of caesium chloride to a liter of the raffinose solution was found to increase the specific rotatory power to $[\alpha]_E = 144.64$ which is the same increase as that produced by potassium chloride.

The experimental data and results are shown above.

7. Results with Potassium Nitrate.

Several runs were made on 1.2 *M* potassium nitrate solution in the presence of 0.08 mol of raffinose, using a silver chloride cathode and rejecting the anode side altogether. Membranes of silk gauze were inserted in the connecting tubes of the stopcocks and a cooling coil was used at the cathode side to increase the density of this portion, in an effort to prevent mixing. In every experiment, however, chloride was found in the middle portions, indicating that mixing had taken place. On account of this mixing it did not seem worth while to complete the analyses. In one case, however, the solutions were analyzed, and it was shown that the ratio of raffinose to water had decreased at the cathode. In other words, the potassium ion carries water with it to the cathode in a potassium nitrate solution or, if one wishes to ascribe the change in the raffinose-water ratio to a complex formed between the chloride ion and the raffinose, then a similar complex must also be assumed in the case of the nitrate ion.

8. Comparison of Degrees of Hydration of the Ions.

For purposes of comparison the transference and hydration data for the four alkali chlorides and hydrochloric acid are summarized in Table I.

¹ Bates, *Bureau of Standards Bulletin* 2, 239.

TABLE I.¹

| Electrolyte (Conc. 1.3 N). | n_w^F/T^c | Δn_w^F | T^c | T_∞^c | T_H^c |
|-------------------------------|---|-----------------|-------|--------------|---------|
| HCl..... | 0.28 \pm 0.04 | 0.24 \pm 0.04 | 0.844 | 0.821 | 0.82 |
| CsCl..... | 0.67 \pm 0.1 | 0.33 \pm 0.06 | 0.491 | 0.491 | 0.485 |
| KCl..... | 1.3 \pm 0.2 | 0.60 \pm 0.08 | 0.495 | 0.495 | 0.482 |
| NaCl..... | 2.0 \pm 0.2 | 0.76 \pm 0.08 | 0.383 | 0.396 | 0.366 |
| LiCl..... | 4.7 \pm 0.4 | 1.5 \pm 0.1 | 0.304 | 0.330 | 0.278 |
| | $N_w^H = 0.28 \pm 0.04 + 0.185 N_w^{Cl}$ (1) | | | | |
| | $N_w^{Cs} = 0.67 \pm 0.1 + 1.03 N_w^{Cl}$ (2) | | | | |
| | $N_w^K = 1.3 \pm 0.2 + 1.02 N_w^{Cl}$ (3) | | | | |
| | $N_w^{Na} = 2.0 \pm 0.2 + 1.61 N_w^{Cl}$ (4) | | | | |
| | $N_w^{Li} = 4.7 \pm 0.4 + 2.29 N_w^{Cl}$ (5) | | | | |

The values of the true transference number of the cation in 1.2 *M* solution (T^c) and at infinite dilution (T_∞^c) as well as the ordinary Hittorf number (T_H^c) appear in the first part of the table. In the second part of the table N_w indicates the average number of water molecules carried by the ion (indicated by the superscript) as it moves through the solution. From Equations 2 and 5 we obtain the relation,

$$N_w^K - N_w^{Cs} = 0.65,$$

or in words, the caesium ion carries on the average 0.65 less molecules of water than the potassium ion and is, therefore, the least hydrated of the alkali ions. If we assign to the chloride ion the hydration values (1) zero and (2) four molecules, the corresponding hydration values for the other ions are shown in Table II.

TABLE II.

| $N_w^{Cl^-}$ | $N_w^{H^+}$ | $N_w^{Cs^+}$ | $N_w^{K^+}$ | $N_w^{Na^+}$ | $N_w^{Li^+}$ |
|--------------|-------------|--------------|-------------|--------------|--------------|
| 0 | 0.3 | 0.7 | 1.3 | 2.0 | 4.7 |
| 4 | 1.0 | 4.7 | 5.4 | 8.4 | 14.0 |

All of the data given above are, of course, based upon the assumption that the raffinose remains absolutely stationary during the passage of the current. There is thus far no evidence indicating that this assumption is invalid to an extent which would appreciably affect the results. With the polarimetric apparatus at present at our disposal it will be possible to work with considerably smaller salt concentrations and also to reduce the concentration of the reference substance as low as 0.01 *M* in the case of lithium chloride solutions. By substituting trehalose for raffinose it will probably even be possible to use a considerably lower concentration than this and thus to remove all reasonable doubt as to the validity of the assumption in question. Work along these lines will be continued in this laboratory.

¹ In this table the values given are the *means* of the two results obtained at each electrode independently:

9. Summary.

1. By transference experiments in the presence of raffinose as a reference substance, the true transference number of caesium ion in 1.2 *M* caesium chloride solution at 25° has been found to be 0.491 and the water transference 0.33 ± 0.06 formula weights of H₂O per faraday, from anode to cathode. Caesium ion is thus the least hydrated of the alkali ions. It carries on the average 0.65 mol less H₂O than potassium ion.

2. Similar experiments with potassium nitrate solutions showed that the water transference was from anode to cathode with this salt also.

3. The effect of caesium chloride upon the specific rotatory power of raffinose is the same as that of potassium chloride. It increases $[\alpha]_D$, 0.09° per mol of salt added to a liter of the 0.1 *M* raffinose solution.

4. Contrary to a statement in the literature, caesium chloride is not appreciably volatile with steam.

URBANA, ILL.

[LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN.]

THE HEAT OF NEUTRALIZATION OF HYDROXYLAMINE AND TETRAMETHYLAMMONIUM HYDROXIDE.

By EMIL O. ELLINGSON.

Received January 29, 1915.

Recent thermochemical measurements by Richards and his co-workers, using the adiabatic calorimeter, have shown conclusively that many of the thermochemical data in the literature are of very questionable accuracy. The adiabatic calorimeter permits a degree of accuracy heretofore unattainable in thermochemical measurements and for the first time puts these measurements on a par with the measurements of other physicochemical constants. Since considerable of the thermochemical data in the literature have been determined by but two investigators (Berthelot and Thomsen), and as the data are often the results of single measurements, by methods which at best could give only approximate values, it has seemed highly desirable that these measurements be repeated, using the methods for precise calorimetry now available.

This paper deals with the measurement of the heat of neutralization of hydroxylamine and tetramethylammonium hydroxide when neutralized with hydrochloric, sulfuric, and trichloroacetic acids in aqueous solutions, using an adiabatic calorimeter. The method followed was practically the same as that used by Richards and Rowe,¹ and the adiabatic bath employed was similar to the one designed by Richards and Burgess² and by Richards and Jesse.³

¹ *Z. physik. Chem.*, **64**, 187 (1908); *Proc. Am. Acad.*, **43**, 475 (1908).

² *THIS JOURNAL*, **32**, 431 (1910).

³ *Ibid.*, **32**, 268 (1910).

Materials.

Trichloroacetic Acid.—A well-known manufacturer's purest trichloroacetic acid was used. The sample taken for the experiments showed but the slightest trace of hydrochloric acid.

Tetramethylammonium Hydroxide.—This base was prepared from recrystallized tetramethylammonium iodide by dissolving the latter in pure water and agitating the solution for several hours at about 45° , with an excess of freshly precipitated silver oxide, avoiding contact with air as much as possible. The warm solution was filtered quickly by powerful suction, through a layer of several filter papers, directly into the container designed for the base. The hydroxide was then carefully standardized by titration with a standard solution of sulfuric acid, using methyl orange as indicator.¹ The strength of the sulfuric acid solution had previously been determined by careful gravimetric analyses.

Hydroxylamine.—Freshly prepared hydroxylamine was used exclusively. The base was made from dry hydroxylamine phosphate $[(\text{NH}_2\text{OH})_3 \cdot \text{H}_3\text{PO}_4]$ by distilling the latter at a low pressure, according to the method of Uhlenhuth.² In this distillation 20 g. of the salt were heated in a fractionating bulb at about 20–30 mm. pressure. The salt decomposed into phosphoric acid and hydroxylamine, the base passing over into the ice-cooled receiver where it solidified. The fraction distilling between 90° and 130° at about 25 mm. pressure was used.

Since hydroxylamine is explosive at higher temperatures, it is necessary to take proper precautions during the distillation.

Strength of Solutions.

Generally the solutions were made up to a concentration approximating, in some cases, to the ratio of one mol of the reagent to fifty of water, and, in other instances, to the ratio of one to two hundred.

Trichloroacetic Acid.—The acid was dissolved in pure, distilled water and the solutions were made up to the desired strength, guided by titration against a standard solution of sodium hydroxide, using methyl orange as indicator.

Hydroxylamine.—The crystalline hydroxylamine, obtained from the decomposition of hydroxylamine phosphate $[(\text{NH}_2\text{OH})_3 \cdot \text{H}_3\text{PO}_4]$, was dissolved in pure, cold water immediately upon the completion of the distillation. The solutions were then made up to the required strength, as indicated by titration against a gravimetrically standardized solution of sulfuric acid, using methyl orange as indicator. The solutions were kept in ice because the base decomposes slowly at the ordinary room

¹ The base exhibited no apparent change of strength on standing for a considerable time, as was indicated by its titration, in the same manner, five months after the experiments herein described were performed.

² *Ann.*, 311, 117 (1900).

temperature. The calorimetric measurements were, therefore, made as soon as possible after standardization of the solutions.

Tetramethylammonium Hydroxide.—The strength of the solution of this base was obtained by titration as previously stated, and the hydroxide was kept in a receptacle adapted to prevent atmospheric carbon dioxide from coming in contact with it.

Method and Apparatus.

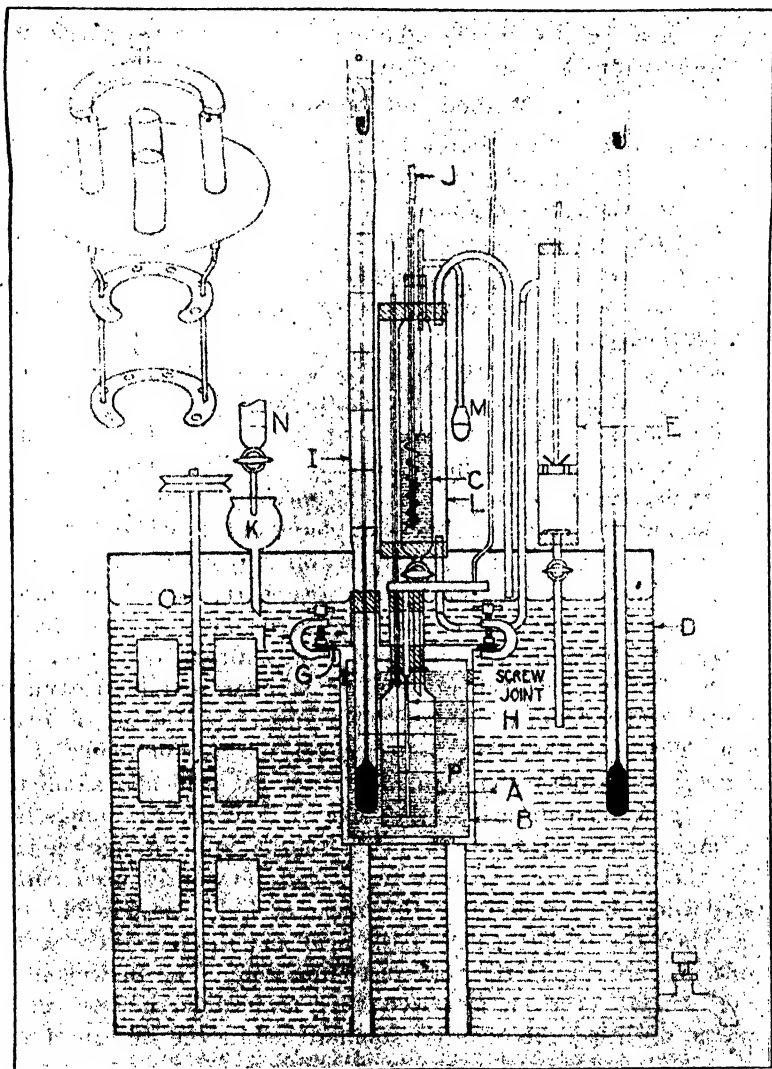
The thermal data were obtained in exactly the same manner as described by Mathews¹ in his experiments on the adiabatic measurements of heats of reaction in nonaqueous solutions. The accompanying diagram represents in cross-section the essential parts of the apparatus. The adiabatic bath D and the necessary fixtures were adjusted in identically the same way as were the corresponding parts of the apparatus used by Mathews.

A weighed quantity (of a known volume) of the solution of the base to be neutralized was placed in the platinum bottle A, which was suspended in a known weight of water contained in the platinum calorimeter B. The quantity of acid required to exactly neutralize the alkali (plus a predetermined amount necessary to compensate for the wetting of the walls and for loss on drainage) was placed in the jacketed, cylindrical compartment C, from which it could be run into A through a stopcock. The acid in C and the base in A were stirred, the former by means of a heavy platinum spiral surrounding the thermometer J, and the latter by a platinum stirrer, P. The water in B was stirred by a silver stirrer, H, attached to two hard-rubber rods. A standardized Beckmann thermometer, I, which could easily be read to 0.001° by the aid of a sliding telescopic lens, was placed in B to register the rise in temperature of the water in the calorimeter. In order that the acid and alkali might be at the same temperature at the time of mixing, the pump E was used to force a strong current of the alkali solution in D through the jacket, L. As the Beckmann thermometer J had previously been carefully compared with the standardized thermometer I, it was possible to determine when the temperatures of the acid and the base were precisely the same, by referring to the table of comparison. The Beckmann thermometer I had been standardized very accurately, in the adiabatic calorimeter, against a thermometer standardized by the Bureau of Standards.

When the acid and the alkali had reached exactly the same temperature, they were quickly mixed by allowing the acid in C to run into the alkali in A, the last drop in the delivery tube of C being forced out by a quick compression of the rubber bulb M. As the temperature in B began to rise, the temperature of the bath D was made to rise by running

¹ THIS JOURNAL, 33, 1291 (1911).

concentrated sulfuric acid from the buret N into the alkali. The flow was so controlled that the temperature in D, as indicated by its thermometer, was always equal to that in B, as shown by the thermometer I.



The solution in D was stirred very thoroughly by a powerful stirrer, O. The stirrers and pump were run by an electric motor at a definite speed throughout all the experiments. The platinum calorimeter B was supported within a closed copper vessel by means of dry cork points, thus avoiding direct contact with the surrounding bath.

In order to calculate the water equivalent of the salt solution resulting from the reaction, the bottle A, with its contents, was weighed after each experiment to ascertain the exact weight of the salt solution. The water equivalent of the solution was then computed from its weight and specific heat, the latter value having been obtained previously by adiabatic measurements.

In every experiment the amount of acid required for the exact neutralization, plus a certain excess to make up for the loss of liquid adhering to the walls of compartment, C, was determined before the actual measurement was made.

TABLE I.

Heat evolved by the neutralization of 40.77 g. of 1.354 *N* hydrochloric acid (gravimetrically standardized) by 2.71 *N* sodium hydroxide.

| | | | | |
|--|-----|------------------------|---|-------------|
| Initial temp. (cor.) of the NaOH in C and of the HCl in A (of the calorimeter)..... | | | | 18.159° |
| Final temp. of the calorimeter (cor.)..... | | | | 19.606° |
| Rise in temperature..... | | | | 1.447° |
| Water in the calorimeter..... | | | | 450.00 g. |
| Wt. of the platinum calorimeter | B | 100.73 g. | | |
| Water equivalent of calorimeter | B = | 100.73×0.0324 | = | 3.264 g. |
| Wt. of the platinum bottle | A | 52.436 g. | | |
| Water equivalent of bottle | A = | 52.436×0.0324 | = | 1.699 g. |
| Wt. of the silver stirrer | H | 23.876 g. | | |
| Water equivalent of stirrer | H = | 23.876×0.055 | = | 1.313 g. |
| Wt. of the platinum stirrer | P | 7.831 g. | | |
| Water equivalent of stirrer | P = | 7.831×0.0324 | = | 0.254 g. |
| Water equivalent of thermometer I = | | | | 2.163 g. |
| Total water equivalent of the calorimeter and fittings..... | | | | 8.693 g. |
| Water equivalent of the 63.02 g. of NaCl solution formed, sp. ht. being 0.95 ¹ | | | | 59.87 g. |
| Total water equivalent = (450 + 98.693 + 59.87) = | | | | 518.563 g. |
| Total heat evolved by the reaction = | | | | |
| 518.56 \times 1.447 = | | | | 750.35 cal. |

The results given in Table II are taken from four experiments conducted to determine the heat liberated as shown in Table I.

TABLE II.

| Total water equivalent. | Initial temp. of acid and base (cor.). | Rise in temp. (cor.). | Total heat liberated. |
|-------------------------|--|-----------------------|-----------------------|
| 518.56 | 18.159° | 1.447° | 750.35 cal. |
| 518.59 | 19.521° | 1.446° | 749.88 cal. |
| 518.61 | 20.203° | 1.446° | 749.91 cal. |
| 518.54 | 18.462° | 1.447° | 750.32 cal. |
| Average, | | | 750.12 cal. |

Hence, by exactly neutralizing 40.77 g. of 1.354 *N* hydrochloric acid by 2.71 *N* sodium hydroxide 750.12 calories of heat are evolved.

¹ Thomsen's value for the specific heat.

TABLE III.

The specific heat of hydroxylamine sulfate $[(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4]$ solution formed by the neutralization of 30.22 g. of 1.0578 *N* hydroxylamine by 1.0607 *N* sulfuric acid. (The approximate molecular ratio of the base or acid to water was 1:50.)

| | |
|--|-------------|
| Wt. of 1.354 <i>N</i> hydrochloric acid..... | 40.77 g. |
| Excess of NaOH solution taken..... | 0.07 cc. |
| Wt. of the hydroxylamine sulfate solution placed in the calorimeter..... | 450.00 g. |
| Initial temp. (cor.) of the NaOH in C and of HCl in A (of the calorimeter)..... | 18.535° |
| Final temp. of the calorimeter (cor.)..... | 20.049° |
| Rise in temperature..... | 1.514° |
| Water equivalent of the 62.96 g. of NaCl solution formed (sp. ht. 0.95) ¹ | 59.81 g. |
| Water equivalent of the calorimeter and fittings (Table I)..... | 8.69 g. |
| Total water equivalent..... | 68.50 g. |
| Total heat absorbed exclusive of the hydroxylamine sulfate solution = 68.50×1.514 | 103.71 cal. |
| Heat liberated by the neutralization of 40.77 g. of 1.354 <i>N</i> hydrochloric acid (Table II)..... | 750.12 cal. |
| Therefore, the total heat taken up by the hydroxylamine sulfate solution = $750.12 - 103.71 = 646.41$ cal. | |
| Specific heat of the solution = $646.41 \div (450 \times 1.514) = 0.9488$ | |

TABLE IV.

Heat evolved by the neutralization of 30.22 g. of 1.0578 *N* hydroxylamine by 1.0607 *N* sulfuric acid. (The molecular ratio of base or acid to water was approximately 1:50.)

| | |
|---|-----------|
| Wt. of hydroxylamine taken..... | 30.22 g. |
| Wt. of sulfuric acid used..... | 30.98 g. |
| Initial temp. (cor.) of the sulfuric acid in C and of the hydroxylamine in A (of the calorimeter)..... | 18.464° |
| Final temp. of the calorimeter (cor.)..... | 19.169° |
| Rise in temperature..... | 0.705° |
| Water in the calorimeter..... | 450.00 g. |
| Water equivalent of the 61.21 g. of hydroxylamine sulfate solution formed, sp. ht. 0.9488 (Table III)..... | 58.08 g. |
| Water equivalent of the calorimeter and fittings..... | 8.69 g. |
| Total water equivalent..... | 516.77 g. |
| Heat evolved by the reaction = $516.77 \times 0.705 = 364.32$ cal. | |
| Since the 30.22 g. of hydroxylamine solution measured 30.08 cc. (at 20°), this amount of heat was liberated by neutralizing $30.08/1000 \times 1.0578 \times 33$ or 1.05 g. of the base in the given concentration. The heat evolved by the neutralization of 1 g. molecule of hydroxylamine will, therefore, be $364.32 \times 33/1.05 = 364.32 \times 31.43 = 11450.5$ cal. | |

The calorimetric procedure consisted in first finding the amount of heat evolved in the neutralization of a definite weight of a certain hydrochloric acid solution by a certain sodium hydroxide solution, the strength

¹ Thomsen's value.

of both being known, using a known weight of water in the calorimeter. This identical reaction was repeated, quantitatively, whenever it was desired to use it as a source of a definite, known amount of heat in measuring the specific heat of the salt solution which was formed in the process of any given neutralization. The water equivalent of the calorimeter and fittings was calculated from the heat capacities of the several parts. The water equivalent of the sodium chloride solution resulting from the neutralization was computed, using Thomsen's value for the specific heat of sodium chloride solution at the given concentration and temperature.

TABLE V.

Results of the measurements of the specific heat of the salt solution formed in the bottle A during the various neutralizations. In each of these determinations 450 g. of the salt solution in question were placed in the calorimeter.

| Salt solution. | Approx. mol. ratio of acid or base to water. | Initial temp. of acid and alkali. | Rise in temperature. | Water equiv- alent. | Specific heat. |
|--|---|--|-------------------------|---------------------------|-------------------|
| NH ₂ OH.HCl..... | 1:50 | 18.854° | 1.510° | 68.54 | 0.9516 |
| | | 18.712° | 1.510° | 68.54 | 0.9516 |
| | | 18.638° | 1.508° | 68.54 | 0.9530 |
| | | | | Mean, | 0.9521 |
| NH ₂ OH.HCl..... | 1:200 | 18.649° | 1.477° | 68.45 | 0.9765 |
| | | 18.664° | 1.478° | 68.50 | 0.9757 |
| | | | | Mean, | 0.9761 |
| (NH ₂ OH) ₂ .H ₂ SO ₄ | 1:50 | 18.535° | 1.514° | 68.50 | 0.9488 |
| | | 18.762° | 1.513° | 68.50 | 0.9495 |
| | | | | Mean, | 0.9491 |
| (NH ₂ OH) ₂ .H ₂ SO ₄ | 1:200 | 18.588° | 1.476° | 68.61 | 0.9769 |
| | | 18.657° | 1.477° | 68.60 | 0.9763 |
| | | 18.596° | 1.475° | 68.55 | 0.9777 |
| | | | | Mean, | 0.9770 |
| NH ₂ OH.CCl ₃ COOH..... | 1:100 | 18.694° | 1.506° | 68.53 | 0.9545 |
| | | 18.726° | 1.507° | 68.59 | 0.9537 |
| | | 18.582° | 1.505° | 68.50 | 0.9553 |
| | | | | Mean, | 0.9545 |
| NH ₂ OH.CCl ₃ COOH..... | 1:200 | 18.684° | 1.479° | 68.50 | 0.9748 |
| | | 18.708° | 1.480° | 68.51 | 0.9741 |
| | | | | Mean, | 0.9744 |
| (CH ₃) ₄ NOH.HCl..... | 1:200 | 18.726° | 1.482° | 68.50 | 0.9726 |
| | | 18.750° | 1.482° | 68.59 | 0.9724 |
| | | | | Mean, | 0.9725 |
| [(CH ₃) ₄ NOH] ₂ .H ₂ SO ₄ | 1:200 | 18.756° | 1.479° | 68.54 | 0.9748 |
| | | 18.715° | 1.479° | 68.52 | 0.9748 |
| | | | | Mean, | 0.9748 |
| (CH ₃) ₄ NOH.CCl ₃ COOH..... | 1:200 | 18.705° | 1.485° | 68.59 | 0.9701 |
| | | 18.657° | 1.487° | 68.60 | 0.9684 |
| | | 18.683° | 1.486° | 68.62 | 0.9693 |
| | | | | Mean, | 0.9693 |

TABLE VI.

| Base and acid and their prox. mol. ratio to water. | Wt. and vol. of solution of base taken. | Wt. of salt solution formed and its sp. ht. | Initial temp. of acid and base. | Rise in temperature. | Total water equivalent. | Heat from reaction. | Heat liberated by one mol. |
|---|---|---|------------------------------------|-------------------------|----------------------------|------------------------|-------------------------------|
| NH ₄ OH | 30.139 g. | 60.79 g. | 18.021° | 0.581° | 516.57 | 300.13 | 9475 cals. |
| HCl | 30.00 cc. | 60.72 | 18.485° | 0.582° | 516.50 | 300.60 | 9490 cals. |
| Mol. ratio | | 60.77 | 18.079° | 0.581° | 516.54 | 300.11 | 9474 cals. |
| | | 60.76 | 18.681° | 0.582° | 516.54 | 300.62 | 9491 cals. |
| | | sp. ht. 0.9521 | | | | Mean, | 9483 cals. |
| NH ₄ OH | 30.0385 g. | 60.21 g. | 18.641° | 0.142° | 517.46 | 73.48 | 9271 cals. |
| HCl | 30.00 cc. | 60.19 | 18.597° | 0.143° | 517.44 | 73.99 | 9335 cals. |
| Mol. ratio | | 60.15 | 18.528° | 0.142° | 517.40 | 73.48 | 9271 cals. |
| | | sp. ht. 0.9761 | | | | Mean, | 9292 cals. |
| NH ₄ OH | 30.220 g. | 61.21 g. | 18.464° | 0.705° | 516.78 | 364.32 | 1450 cals. |
| H ₂ SO ₄ | 30.08 cc. | 61.18 | 18.694° | 0.705° | 516.76 | 364.31 | 1450 cals. |
| Mol. ratio | | 61.20 | 18.607° | 0.704° | 516.78 | 363.81 | 1435 cals. |
| | | sp. ht. 0.9491 | | | | Mean, | 1445 cals. |
| NH ₄ OH | 30.035 g. | 60.38 g. | 18.729° | 0.171° | 517.68 | 88.52 | 1070 cals. |
| H ₂ SO ₄ | 29.95 cc. | 60.47 | 18.792° | 0.171° | 517.77 | 88.54 | 1072 cals. |
| Mol. ratio | | 60.40 | 18.577° | 0.171° | 517.70 | 88.53 | 1071 cals. |
| | | sp. ht. 0.9770 | | | | Mean, | 1071 cals. |

| | | | | | | | | |
|-----------------------------|-----------------|------------|----------------|---------|--------|--------|-------|-------------|
| NH_4OH | 0.5266 <i>N</i> | 30.0735 g. | 61.21 g. | 18.565° | 0.296° | 517.11 | 53.06 | 9670 cals. |
| CCl_3COOH | 0.5243 <i>N</i> | 30.05 cc. | 61.16 | 18.644° | 0.296° | 517.07 | 53.05 | 9670 cals. |
| Mol. ratio | 1:100 | | 61.18 | 18.678° | 0.297° | 517.09 | 53.57 | 9702 cals. |
| | | | ip. ht. 0.9545 | | | | Mea | 9681 cals. |
| NH_4OH | 0.2642 <i>N</i> | 30.0385 g. | 60.84 g. | 18.598° | 0.142° | 517.97 | 73.55 | 9280 cals. |
| CCl_3COOH | 0.2621 <i>N</i> | 30.00 cc. | 60.90 | 18.649° | 0.142° | 518.03 | 73.56 | 9281 cals. |
| Mol. ratio | 1:200 | | 60.85 | 18.619° | 0.142° | 517.97 | 73.55 | 9280 cals. |
| | | | ip. ht. 0.9744 | | | | Mea | 9280 cals. |
| $(\text{CH}_3)_4\text{NOH}$ | 0.2660 <i>N</i> | 30.027 g. | 60.64 g. | 18.726° | 0.194° | 517.66 | 00.43 | 12594 cals. |
| HCl | 0.2639 <i>N</i> | 29.98 cc. | 60.70 | 18.781° | 0.195° | 517.72 | 00.95 | 12659 cals. |
| Mol. ratio | 1:200 | | 60.68 | 18.694° | 0.195° | 517.70 | 00.95 | 12659 cals. |
| | | | ip. ht. 0.9725 | | | | Mea | 12637 cals. |
| $(\text{CH}_3)_4\text{NOH}$ | 0.2660 <i>N</i> | 30.027 g. | 60.46 g. | 18.729° | 0.222° | 517.63 | 14.91 | 14410 cals. |
| H_2SO_4 | 0.2651 <i>N</i> | 29.98 cc. | 60.42 | 18.761° | 0.223° | 517.59 | 15.42 | 14474 cals. |
| Mol. ratio | 1:200 | | 60.42 | 18.712° | 0.222° | 517.59 | 14.90 | 14408 cals. |
| | | | ip. ht. 0.9748 | | | | Mea | 14431 cals. |
| $(\text{CH}_3)_4\text{NOH}$ | 0.2660 <i>N</i> | 30.027 g. | 61.92 g. | 18.700° | 0.194° | 518.71 | 00.63 | 2619 cals. |
| CCl_3COOH | 0.2621 <i>N</i> | 29.98 cc. | 61.81 | 18.678° | 0.194° | 518.60 | 00.61 | 2616 cals. |
| Mol. ratio | 1:200 | | 61.84 | 18.774° | 0.194° | 518.63 | 00.62 | 2617 cals. |
| | | | ip. ht. 0.9693 | | | | Mea | 2617 cals. |

The second step concerned itself with the measurement of the heat liberated when neutralizing a definite weight of a given base by a certain acid, the exact strength of each solution being known, and the same amount of water being placed in the calorimeter as before. Since a knowledge of the water equivalent of the salt solution formed in any neutralization was indispensable, it became necessary to measure the specific heat of such solution.

Hence the third step consisted in measuring the specific heat of the salt solutions formed. This value was obtained by substituting, in the calorimeter, an equal weight of the salt solution in question for the water originally used in it, and then repeating the neutralization of the hydrochloric acid with the sodium hydroxide to liberate an exact, known amount of heat as described above.

The preceding results are given to illustrate the method and calculation involved (Tables I, III, IV).

The final data for the heat liberated by the neutralization of solutions of hydroxylamine and tetramethyl ammonium hydroxide by solutions of hydrochloric, sulfuric, and trichloroacetic acids are tabulated in Table VI.

It will be noticed, in Table VI, that the heat of neutralization of a given base decreases considerably with the increase in the dilution of the solutions. Thus, the heat evolved when hydroxylamine acted on hydrochloric acid, in a molar concentration of 1 to 50, was 191 calories higher than when the reaction took place in a concentration of 1 to 200. Similarly, when the same base acted on sulfuric acid, in a concentration of 1 to 50, 374 calories more were liberated than when the reaction occurred in a concentration of 1 to 200. Again, when this base was neutralized by trichloroacetic acid, in the ratio of 1 to 100, 401 calories more were given off than when the neutralization took place in the ratio of 1 to 200. The table also shows that the heats of neutralization of trichloroacetic and hydrochloric acids with a given base were approximately the same for the dilution of 1 to 200. For convenience in comparing these results Table VII is given. The corresponding values obtained by Thomsen are given in brackets.

TABLE VII.

| NH ₂ OH + HCl. | | NH ₂ OH + CCl ₃ COOH. | | NH ₂ OH + 1/2 H ₂ SO ₄ . | |
|--|-----------------|--|-----------------|--|-----------------|
| Conc. | Heat liberated. | Conc. | Heat liberated. | Conc. | Heat liberated. |
| 1:50 | 9483 cals. | 1:100 | 9681 cals. | 1:50 | 11445 cals. |
| 1:200 | 9292 cals. | 1:200 | 9280 cals. | 1:200 | 11071 cals. |
| | [9260] | | | | [10790] |
| (CH ₃) ₄ NOH + HCl. | | (CH ₃) ₄ NOH + CCl ₃ COOH. | | (CH ₃) ₄ NOH + 1/2 H ₂ SO ₄ . | |
| 1:200 | 12637 cals. | 1:200 | 12617 cals. | 1:200 | 14431 cals. |
| | [13745] | | | | [15515] |

The thermal effect due to a definite amount of dilution in the sulfate

was nearly twice that produced in the chloride by the same amount of dilution, whereas the thermal change in the trichloroacetate, caused by a dilution only half as great, was considerably larger than that brought about in the sulfate.

The values for the heats of neutralization of hydroxylamine are approximately the same as Thomsen's, our figures ranging from 0.3% to 2.6% higher. In the case of tetramethylammonium hydroxide, however, the values obtained are about 7.5% lower than Thomsen's. No data on the heats of neutralization of the two bases with trichloroacetic acid have been found in the literature for comparison.

The results recorded in this paper are believed to possess an unusually high degree of precision, and yet, such results are to be expected from the exact method of calorimetry employed.

Summary.

1. The heats of neutralization of hydroxylamine and tetramethylammonium hydroxide when neutralized by hydrochloric, sulfuric, and trichloroacetic acids, in aqueous solutions, have been measured adiabatically.

2. The results obtained for hydroxylamine are from 0.3% to 2.6% higher and for tetramethylammonium hydroxide about 7.5% lower than Thomsen's values for the same bases (Table VII).

3. The heats of neutralization of hydroxylamine and tetramethylammonium hydroxide with trichloroacetic acid have been measured for the first time, as far as we are aware.

In conclusion the writer wishes to express his obligation to Professor J. H. Mathews for helpful suggestions as well as for aid in obtaining the apparatus used.

MADISON, WIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE.]

A CRITICISM OF THE ELECTRON CONCEPTION OF VALENCE.

By ROGER F. BRUNEL.

Received January 18, 1915.

Physical investigations of recent years have convinced most chemists that atoms of all elements contain, if they are not made up of, negative electrons, held in position by a positive charge. The attractive force between atoms is thus electrical in origin. This view is shared by the author.

In 1909, Nelson, Beans, and Falk¹ published an article developing the idea that "every chemical bond formed between two atoms involves the transfer of a corpuscle from one atom to the other,"² a conception for which

¹ *School Mines Quart.*, 30, 179 (1909).

² *THIS JOURNAL*, 35, 1810 (1913).

J. J. Thomson¹ was originally responsible, although he has now abandoned it. The resulting electrostatic charges are apparently considered responsible for the interatomic attraction. This conception is now commonly referred to in THIS JOURNAL as the "Electron Conception of Valence," and has been extensively developed by Nelson, Beans, and Falk, Fry, L. W. Jones and others.² According to this hypothesis chemical bonds are to be represented as $\text{Cl} \rightarrow \text{Cl}$, $\text{C} \rightarrow \text{C}$, $\text{H} \rightarrow \text{Cl}$, or $\text{Cl}^+ \text{---}^- \text{Cl}$, etc. This hypothesis is by no means generally accepted, as is the fundamental conception of the electrical constitution of the atom, and is by no means a necessary corollary of that.

Objections to this conception from the physical point of view, all of which appear to the author to be valid, have recently been brought forward by Bates.³ Bray and Branch,⁴ Lewis,⁵ and Arsem,⁶ have recently proposed other hypotheses dealing with the same question, and Thomson⁷ now offers quite a different explanation of the manner of chemical union. Some of these views will be referred to further below. The object of this paper is to call attention to certain weaknesses in the arguments put forward in support of this conception and certain difficulties that arise in applying it to chemical phenomena.

The development and application of this conception have involved the formulation of several supplementary hypotheses, and we must turn to the earlier papers on the subject for direct arguments, based on simple phenomena, for the fundamental assumption on which it is based. I would first call attention to certain of these arguments, advanced by Nelson, Beans, and Falk.⁸

(a) These authors note that according to their hypothesis ethane must have the unsymmetrical structure $\text{H}_3\text{C}^+ \text{---}^- \text{CH}_3$. To meet the objections likely to be called forth from the organic chemist by such an assumption, it is stated that one substance, triphenylmethyl, shows evidence of such a polar structure in that it forms a conducting solution in sulfur dioxide, where these authors assume that the ions $(\text{C}_6\text{H}_5)_3\text{C}^+$ and $(\text{C}_6\text{H}_5)_3\text{C}^-$ are present.

In the first place this assumes one of the points at issue, for the ad-

¹ *Phil. Mag.*, [6] 7, 237.

² References to numerous papers on this subject will be found in THIS JOURNAL, 35, 1813 (1913); and 36, 1035 (1914).

³ THIS JOURNAL, 36, 789 (1914).

⁴ *Ibid.*, 35, 1440 (1913).

⁵ *Ibid.*, 35, 1448.

⁶ *Ibid.*, 36, 1655.

⁷ *Phil. Mag.*, [6] 27, 757 (1914).

⁸ *School Mines Quart.*, 30, 179 (1909). Practically the same arguments are to be found in THIS JOURNAL, 32, 1637 (1910).

vocates of the theory have first to offer proof that the ability of a substance to split into charged ions in solution is evidence that the dissociating parts are already charged in the molecule before dissociation occurs.

But, furthermore, there is little evidence that the ionization of triphenylmethyl is of the sort indicated, the present tendency being, in the case of nonaqueous solvents at least, to assume the ionization of some complex formed with the solvent. Gomberg¹ assumed that triphenylmethyl ions are present in sulfur dioxide solution, but with no direct evidence except that he noted the similarity between this case and the formation of conducting solutions of bromine in various solvents, especially in sulfur dioxide. Such an argument loses its force in view of the recent investigations of Bruner and Galecki,² and Bruner and Bekier,³ who obtained evidence that in solutions of bromine, and iodine, ICl and ICl_3 , in nitrobenzene and sulfur dioxide no halogen kations are present.

Schlenck⁴ has also shown that although triphenylmethyl sodium forms a conducting solution in ether, it cannot be due to dissociation in the sense $(\text{C}_6\text{H}_5)_3\text{C} + \text{Na}$, but rather to the ionization of some more complex molecules formed in the solution.

The ionization in these cases is thus of a more complex sort than at first appears, and at the present stage of our knowledge of such phenomena can hardly furnish proof that in sulfur dioxide solution of triphenylmethyl we have the ions assumed by Nelson, Beans, and Falk. In general, we can certainly say that in organic compounds there is not the slightest evidence of such polarity as is demanded by this theory on the part of the carbon atoms.

(b) The next use made of the directed valences is in explaining the well-known fact that the melting points of the homologous series of $\omega\omega'$ saturated dibasic acids fall on a zigzag curve, those of alternate members of the series being lower than those of the preceding and following members. An explanation is proposed which is based on the presence of similar groups at the ends of the carbon chain. This results in alternate symmetrical and unsymmetrical valence structures for the members of the series, which might be responsible for alternate high and low melting points. These authors suggest that the same may be found to hold true for the series of monobasic acids, for which, they remark, the electronic formulas cannot yet be written. The last remark is not particularly convincing, since it would appear that we know as much about the monobasic acids as about their more complex dibasic relatives. The fact that the melting points

¹ *Ber.*, 37, 2050 (1904).

² *Z. Physik. Chem.*, 84, 513 (1913).

³ *Ibid.*, 84, 570.

⁴ *Ber.*, 47, 1678 (1914).

of the monobasic acids do fall on a zigzag curve¹ exactly similar to that for the dibasic acids appears to invalidate the argument for the "electron conception valence" based on the latter, since the explanation proposed for the dibasic acids rests fundamentally on the presence of similar groups at both ends of the carbon chain and would demand a smooth curve for the monobasic acids.

Furthermore, if we examine other homologous series we find, in as far as data are available in the latest edition of the Richter Lexikon, similar zigzag melting point curves for the ethyl esters of monobasic acids, for the amides of dibasic acids, and for the $\omega\omega'$ -glycols; a smooth curve for the monohydric alcohols; a curve with a minimum point for the n -aldoximes and for the dialkylsulfones; and an altogether irregular curve for the amides of monobasic acids. Even allowing for errors in melting points of less easily accessible compounds, it is not evident that there is justification for choosing one homologous series from this group and basing on it an argument for the valence hypothesis. Thus the proposed explanation of the zigzag curve of the dibasic acids is misleading.

(c) Double bonds between carbon atoms are next taken up. Of the three possible formulas, \longleftrightarrow , \Rightarrow , and \Leftarrow , \rightleftharpoons is chosen as the stable arrangement from the fact that the stable hydrocarbon, propene, gives, on treatment with hydriodic acid, a mixture of primary and secondary propyl iodides. Since the iodine (negatively charged) goes partly to each carbon atom it is assumed that there must be positive ends of bonds on both carbon atoms, indicating the formula $\text{CH}_3\text{CH} \rightleftharpoons \text{CH}_2$. Since this reaction is offered as evidence for assuming a symmetrical distribution of the positive and negative charges between the two unsaturated carbon atoms, it is somewhat surprising on examining the quantitative data to discover that over 99.5% of the product of the reaction is the secondary propyl iodide. The authors tell us that this is due to the influence of the methyl group. The addition of ClBr and ClI to propene is somewhat better, the ratio of the two possible addition products being 7 : 5 and 4 : 1, respectively. These reactions furnish the entire basis for determining how the double bond is to be written in all stable compounds with the ethylene linkage. It is not evident to the author how the above facts furnish any reason for assuming any connection whatever between the direction of the valences and the course followed by such addition reactions.

Furthermore, the addition of halogen acids to alkenes is a still more perplexing matter than is here implied. The author has investigated extensively the addition of hydrobromic acid to isobutene, and has ob-

¹ Levene and Jacobs, *J. Biol. Chem.*, 18, 463 (1914) have recently published data for the m. ps. of the acids C_{11} - C_{18} which assign to the acid C_{11} a higher value than that of C_{14} . The melting point curve for the series therefore loses its zigzag character at this point, but retains it elsewhere.

tained by this process products containing all the way from 0% to 55% of isobutyl bromide, the remainder being tertiary bromide, depending upon experimental conditions. A reaction which may be subject to such wide variation can be of little value as evidence for any valence hypothesis.

(d) The theory is applied to double bond isomerism of the maleic-fumaric type. The most obvious objection to this application, namely, that three isomers are in general predicted by the theory whereas in nearly all cases only two are known, is forestalled by the statement of the authors that the prediction of unknown facts by a theory is a far less serious fault than the failure to account for known ones, and the convenient assumption that all the predicted but unknown isomers are very unstable if not incapable of isolation. There must surely be limits beyond which this attitude becomes unsafe. But to the theory even with these elastic reservations, there are objections.

The case of the cinnamic acids, referred to by Nelson, Beans and Falk as one where the expected number of isomers exist, has now become rather an argument against their hypothesis, since the existence of four isomers has been established, the theory calling for three, while the recent work of Stobbe and Schönburg¹ has shown them not to be due to polymorphism, but, apparently, to chemical isomerism.

There is also further objection to the use of the theory for this type of isomerism. In the preceding argument, (c), the formula for propene is deduced from its behavior on addition of hydriodic acid, the assumption being made that the iodine tends to unite with such carbon atoms as carry the positive ends of valences, that is, positive charges. The isomeric unsaturated acids (maleic-fumaric type) are now assumed to differ in the directions of their valences, \rightleftharpoons , and \Rightarrow . If the argument applied to propene is of any significance, then the isomeric unsaturated acids must give different addition products with halogen acids. Unfortunately it is with the halogens that such so-called geometrical isomers give isomeric addition products (stereoisomeric products), whereas it is well known that with halogen acids the addition products are the same from both members of such a pair.² It is impossible to see the slightest ground for the use of these polar valences in connection with this type of isomerism.

(e) The existence of unexplained isomeric nitrotoluenes and other compounds described by Ostromisslensky³ is accounted for by isomerism of the above type in the benzene ring. In view of our slight knowledge as to the nature of such isomerism the case can hardly be discussed profitably. The Kekulé theory would explain it as satisfactorily.

¹ *Ann.*, 402, 187 (1913).

² Michael and Freer, *J. prakt. Chem.*, N. F., 40, 95. and Michael, *Ibid.*, 40, 171 (1889).

³ *Z. physik. Chem.*, 57, 341 (1907).

(f) When it comes to application of the conception to the behavior of compounds with the acetylene union, it will first be necessary to explain some of the inconsistencies noted under (d) and formulate a somewhat exact system of hypotheses before the discussion can be profitable.¹

The paper from which the above illustrations are taken takes up numerous other organic problems—the diazo compounds, tautomerism, etc., but little more is shown than that the formulas of the compounds could be written in this new nomenclature, the problems being complex ones and the theory elastic.

The further the electron conception of valence is developed the more qualifying factors we have to admit. In a later paper,² Falk presents a classification of the unsaturated acids, in the attempt to show that when the bonds of the unsaturated linkage are directed in certain ways the affinity constants of the acids fall within certain limits.

The value of the classification in itself or as evidence for the valence theory, however, becomes small when we note that outside of a rather restricted number of compounds the values of the affinity constants depart widely from those predicted. This is attributed to "constitutive influences." But if this new theory of chemical combination contributes nothing to the elucidation of this large unknown factor of organic chemistry, it becomes still more difficult to find proof for it in its application to the more complex problems.

Most applications of the electron theory of valence have been in connection with some of the most perplexing questions of organic chemistry. We are, however, not justified in applying a hypothesis merely because it provides a convenient method of formulating or even of correlating a limited number of phenomena, if it is inconsistent as soon as we step outside narrow limits, or if it is not fundamentally suited to explain the manner of chemical combination. The author has little sympathy with the statement of Falk³ that its "convenient symbolism alone... would justify its use in practical work." This conception of valence involves necessarily certain assumptions regarding the nature of union between atoms and the mechanism of chemical reactions, and there are certain questions to which I would call attention.

The statement is made by W. A. Noyes⁴ that "all reactions involving decomposition of molecules are preceded by an ionization of the parts of

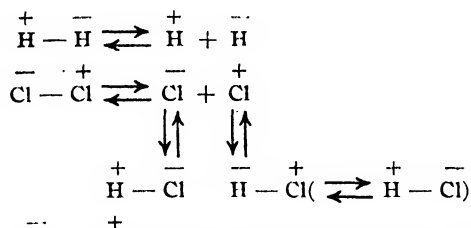
¹ Only a slight examination of the somewhat confusing relations between the isomeric unsaturated acids and the corresponding saturated compounds is needed to show how superficial are the arguments put forward by Falk for the application of the electron conception of valence to the various types of unsaturated compounds.

² THIS JOURNAL, 33, 1140 (1911).

³ *Ibid.*, 35, 1811 (1913).

⁴ *Ibid.*, 23, 460 (1901). An interesting discussion of this question is to be found in the article by Berthoud, *J. chim. phys.*, 10, 578 (1912).

the molecule," and this view is evidently adopted by other advocates of this conception. Thermal dissociation of such molecules as hydrogen, hydrogen chloride, phosphorus pentachloride, etc., is thus assumed to yield primarily charged atoms or radicals. Let us examine the reaction between hydrogen and chlorine, as formulated by Fry.¹ The bracketed reaction appears to be implied and is added by the author. The decomposition of hydrogen chloride would, of course, involve the reversal of these steps.



The electromer $\overset{-}{\text{H}} - \overset{+}{\text{Cl}}$ must be present in traces only, since otherwise there is no reason why it should not ionize in solution, and why, for example, chlorine should not appear at the cathode in electrolysis. This electromer is thus very unstable.

Let us consider the following question: Why does HCl exist in preference to the system $\text{H}_2 + \text{Cl}_2$? Instead of saying that H and Cl atoms have a greater affinity for each other than for other atoms of their own sort, the electron conception of valence would enable us to be more specific and state that H and Cl have a great tendency, respectively, to lose and gain an electron. Here we are apparently nearly touching upon Abegg's "electroaffinity," although he assumed atoms to become charged only when ionization occurred.

One of the fundamental problems of chemistry is surely the determination or exact specification of the relative tendencies of various sorts of atoms to combine with each other, but it is not certain that we are greatly assisted by restating the problem as that of determining the relative tendencies of atoms to gain and lose electrons from each other. The somewhat puzzling stability of the hydrogen and chlorine molecules is not explained merely by writing signs above the atoms. Nor can we so easily escape the conflicts that arise in trying to assign relatively positive and negative characters to different elements. For example, if chlorine and hydrogen combine with each other for the reason suggested above, we must also expect that chlorine would combine with any element somewhat more or less negative than itself more energetically than with itself, but the properties of oxides of chlorine or of Br-Cl do not bear out this expectation.

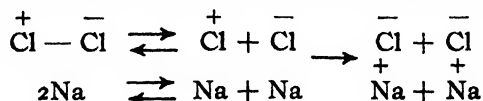
If we look further into this question of the relative tendencies of differ-

¹ THIS JOURNAL, 23, 263 (1914).

ent atoms to gain and lose electrons, we have not to go far to find inconsistencies among the electronic formulas. For example, we find, according to Jones¹ that the compound $(\text{CH}_3^+)_3 \equiv \text{N}^+ \begin{smallmatrix} + \\ \text{---} \end{smallmatrix} \begin{smallmatrix} \text{Cl} \\ \text{---} \end{smallmatrix} \text{OH}$ changes to $(\text{CH}_3^+)_3 \equiv \text{N}^+ \begin{smallmatrix} + \\ \text{---} \end{smallmatrix} \text{Cl}$, the chlorine taking two electrons from the nitrogen. The compound $(\text{Cl}_3^-) \begin{smallmatrix} + \\ \text{---} \end{smallmatrix} \text{P}^+ \begin{smallmatrix} + \\ \text{---} \end{smallmatrix} \text{Cl}$ exists in equilibrium with $(\text{Cl}_3^-) \begin{smallmatrix} + \\ \text{---} \end{smallmatrix} \text{P}^+ \begin{smallmatrix} + \\ \text{---} \end{smallmatrix} \text{Cl}$. The compound $(\text{CH}_3^+)_3 \equiv \text{N}^+ \begin{smallmatrix} + \\ \text{---} \end{smallmatrix} \text{Br}$, however, is assumed not to change to $(\text{CH}_3^-) \equiv \text{N}^+ \begin{smallmatrix} + \\ \text{---} \end{smallmatrix} \text{Br}$. We must conclude, then, that bromine has less tendency than chlorine to take an electron from nitrogen, that it is less negative.² Similarly the compound $(\text{CH}_3^+)_3 \equiv \text{N}^+ \begin{smallmatrix} + \\ \text{---} \end{smallmatrix} \text{OH}$ is quite stable. OH has thus also less tendency than chlorine to take an electron from nitrogen, that is, like bromine, it is less "negative" than chlorine. This conclusion is, however, contradicted by the assumption made throughout this paper by Jones and in other articles dealing with this subject, that the stable form of hypochlorous acid is $\text{HO} \begin{smallmatrix} - \\ \text{---} \end{smallmatrix} \text{Cl}$, the OH having taken an electron from the chlorine. It is here assumed to be more "negative" than chlorine. I shall mention this compound again below.

A hypothesis which deals with the nature of the attractive force between atoms contains inevitably expressed or implied assumptions regarding chemical affinity. If our above assumptions in connection with the hydrogen chloride equilibrium are incorrect, *then there is plainly great need of some explicit statement as to what principles do control the gain and loss of electrons, and how this property is related to chemical affinity.* With the whole theory in its present vague state, a multitude of contradictory hypotheses can easily be hidden by the complex and elastic nomenclature.

Since the algebraic sum of the positive and negative charges in any chemical compound or system must, according to our fundamental conception, be zero, it naturally follows that we shall never be at a loss to properly arrange the charges so that any ions may interact, provided we assume the proper exchanges of electrons. The reaction, sodium plus chlorine, would be somewhat different from that examined above.³

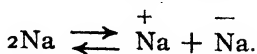


Evidently we must assume that one chlorine takes an electron from each of the two sodium atoms; or we may assume that we have

¹ THIS JOURNAL, 36, 1268 (1914).

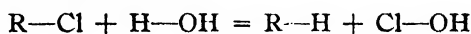
² There is opportunity for confusion of terms here. By a "negative" atom is meant one tending to become negatively charged, the customary usage. This will of course be one tending to gain an electron, *i. e.*, one which before it gains the electron is presumably as a whole, or at some point, strongly positive.

³ Other simple reactions are formulated by Fry, THIS JOURNAL, 36, 267 (1914).



In this reaction and that between hydrogen and chlorine two assumptions are involved which must constantly be employed in applying the electron conception of valence. First, we assume a great mobility on the part of the electrons—such, in fact, that the nonexistence of the hypothetical less stable electromers is not surprising. Secondly, we assume the existence, always, in equilibrium, of all the possible electromers.

Once, however, these assumptions are admitted, all plausibility disappears from those arguments commonly employed by the advocates of the theory, in which the charge on some atom in a compound is deduced from the charge judged to be present on it after the compound has been subjected to a reaction of some sort. For example, hypochlorous acid, supposed to be $\overset{-}{\text{HO}}-\overset{+}{\text{Cl}}$ is a substance commonly used for reference. If a compound, say RCl , reacts thus:



it is concluded that the chlorine, positive in $\overset{+}{\text{Cl}}-\text{OH}$, must also be positive in $\text{R}-\overset{+}{\text{Cl}}$, thus $\text{R}-\overset{+}{\text{Cl}}$.¹

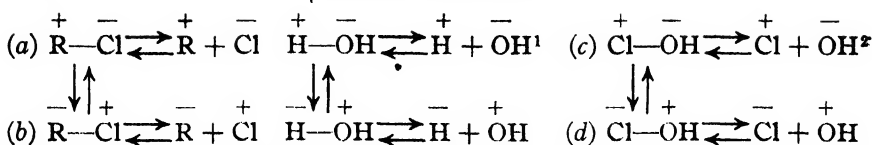
In the first place we must inquire further into the reasons for supposing hypochlorous acid to be necessarily $\overset{+}{\text{Cl}}-\text{OH}$. Oxygen is not necessarily negative any more than is chlorine. In fact, from its position in the periodic system, which according to Falk² must furnish the basis for distribution of the charges in the simpler compounds, we should expect it to be less inclined to carry the negative charge than chlorine. Here, where it has already gained one electron from the hydrogen, its tendency to take another should be rather decreased than increased. Why, then, is not the stable form of hypochlorous acid $\overset{-}{\text{Cl}}-\overset{+}{\text{OH}}$ rather than $\overset{+}{\text{Cl}}-\overset{-}{\text{OH}}$? There hardly appears to be justification for the certainty with which Fry states³ that "to admit the existence of hypochlorous acid is to admit the existence of positive chlorine." We must ask again what principle is supposed to control this gain and loss of electrons.

But, assuming the formula $\overset{+}{\text{Cl}}-\overset{-}{\text{OH}}$ to be correct, we must note that the substances reacting in the above equation are really to be represented as

¹ This type of argument is commonly employed, for example in two articles by Fry, *THIS JOURNAL*, 36, 248 and 262 (1914); Nelson, Beans and Falk, *Ibid.*, 35, 1816 (1913) designate such hydrolytic reactions as one of the chief means for determining the charges present on atoms.

² *THIS JOURNAL*, 32, 1637 (1910).

³ *Ibid.*, 36, 267 (1914).



With this scheme as a basis there will be no difficulty in explaining the formation of compound (d) from compound (b), or of (c) from (a). Assuming the formula of HOCl to be known it is clear that we cannot draw conclusions as to the formula of our compound RCl. Further conclusions as to which of the ions present are reacting with each other will appear to depend upon assumptions, based on analogy, as to the relative affinity of various radicals for each other, just such as most organic chemists employ, expressed in some terms or other.

In view of these supplementary hypotheses which the electron conception of valence has come to demand, which permits us to distribute the electrons largely in accordance with the exigencies of the particular equation in hand it appears to the author to have developed into merely a new system of nomenclature, desirable, if correct, but as far without direct support. This complex array of hypothetical electromeric substances does not appear to be an acquisition to the science which is desirable in itself.

Of the other applications of the theory to more complex problems the author would mention only that of Fry³ to the question of substitution in the benzene ring. The rule governing the position of substituents which Fry puts forward with the utmost confidence⁴ is so simple as to arouse distrust at once. It would appear sufficient to say that in view of the extensive investigations carried on in this field in recent years by Hollemann, Flürscheim, Obermiller and others, if any such simple rule could cover the facts it would have been discovered long ago empirically, even if not expressed in the same terms. Hollemann⁵ has, however, recently called attention to a number of cases of substitution reactions where it is quite impossible to apply Fry's rule.

Bray and Branch,⁶ and Lewis⁷ have recently advocated the view that there are both "polar" and "nonpolar" bonds. Certain difficulties appear to lie in this hypothesis, one of them being that mentioned by Nelson and Falk⁸ of determining which bonds are polar and which not. Additional

¹ Jones, *THIS JOURNAL*, **36**, 1277.

² *Ibid.*, 1282.

³ *THIS JOURNAL*, **36**, 248 (1914).

⁴ *Ibid.*, p. 252.

⁵ *Ibid.*, **36**, 2495.

⁶ *Ibid.*, **35**, 1440 (1913).

⁷ *Ibid.*, **35**, 1448.

⁸ *Ibid.*, **36**, 209 (1914).

hypotheses will also be needed in explaining such a reaction as a double decomposition between a polar and a nonpolar compound.

Lewis¹ gives a list of the characteristics of compounds with polar and nonpolar bonds, from which it is clear that no sharp dividing line exists. It does not appear altogether clear just how we are to conceive of bonds representing a gradation between the polar and nonpolar condition, particularly as regards their behavior in chemical transformations.

The chief reason prompting Lewis to favor polar bonds appears to be the desire to represent certain compounds as having a very indefinite and mobile molecular structure. What value this conception may have in itself can hardly be clear until it is developed further, but the author questions whether, if adopted, it involves necessarily the assumption of polar bonds.

The recently expressed view of J. J. Thomson² also employs the conception that the exchange of an electron occurs between certain atoms in certain molecules, this phenomenon being designated as intramolecular ionization; but it is to be noted that in such cases it is not a step necessary to the union of the atoms but a phenomenon, so to speak, superimposed on that. Furthermore it is evidently considered to be the exceptional rather than the usual occurrence in the case of atomic unions. The union of atoms through electrical forces is satisfactorily accounted for without it.

Thomson's reason for assuming such intramolecular ionization lies in the attempt to account for the high dielectric constants of certain substances and the fact that these dielectric constants depart from the value predicted by the rule of Maxwell expressing a relation between dielectric constant and square of the refractive index. The high dielectric constants of the substances are accounted for by the high electric moments of the molecules, and these in turn are attributed to transfers of electrons within the molecule.

It does not appear certain, however, that the large electrical moments of some molecules could not be accounted for in some other way. We are here on rather speculative ground from the physical point of view; and in a field where many assumptions would be possible, in view of the complex system of electrical charges which the molecule, according to Thomson's conception, will represent, we can hardly look for conclusive evidence for the phenomenon of "intramolecular ionization." Thomson's basis for the classification of "polar" and "nonpolar" compounds is also such that, as with that of Lewis, a sharp dividing line between the two will not appear.

Nelson and Falk³ raise other objections to the conception of both

¹ *Loc. cit.*, p. 1450.

² *Phil. Mag.*, [6] 27, 757 (1914).

³ *THIS JOURNAL*, 36, 210 (1914).

polar and nonpolar bonds, and since one of these would be as well an objection to a theory involving no polar bonds I shall refer to it here. They note that this view would represent the gradual oxidation of methane to carbon dioxide as a series of steps without any change in the charges on the carbon atom, and they remark that such a supposition is untenable. This statement is somewhat too categorical in view of the fact that it is only the assumptions involved in the theory they are defending that render it untenable. If we choose to assume no charges on the carbon, the picture of the oxidation process is moderately satisfactory. It is the definition of oxidation put forward by the advocates of the electron theory, based on the behavior electrolytes in aqueous solution, which necessitates the assumption of the charges on the carbon.

There appears to be little justification for any very dogmatic statements regarding the oxidation of methane. The oxidation of Fe'' to Fe''' in aqueous solution is, for example, a process in which we suppose a change in the electric charge on the ions is concerned. But as far as the molecular forms of the reacting substances are concerned, we can only say that FeCl_2 is gradually replaced by FeCl_3 . It is quite an unproved assumption that the charges are still present on the iron in the undissociated molecules, except in as far as the advocates of this theory have proved it; it is then also an assumption that the change of FeCl_2 to FeCl_3 could not be brought about except by a process involving ionization and changes in which electric charges are concerned. It is thus also an assumption that anything ionic is involved in the replacement of the hydrogen of methane by oxygen. There appears to be in the paper of Falk and Nelson an underlying desire to consider all reactions ionic because some are. But it appears doubtful whether most, or even very many chemists are prepared to adopt this position. The tendency among organic chemists appears to be rather in the opposite direction, since the view long advocated by Michael that the first step in chemical reactions is the formation of a complex molecule by the reacting substances has recently been taken into consideration by numerous investigators, for example, Fischer,¹ Kauffmann,² Gadamer,³ Schmidlin,⁴ Baume,⁵ Berthoud,⁶ and others. Electrolytic dissociation is thus considered as a special phenomenon occurring with certain substances in certain solvents. Furthermore, the process of electrolytic dissociation, even when it occurs, is no longer regarded as necessarily the step through which the electrolyte reacts, as is evidenced by many recent investigations of Acree, Stieglitz, Bredig and others.

¹ *Ann.*, 394, 350 (1913).

² *Die Valenzlehre*, p. 336 (1911).

³ *J. prakt. Chem.*, [2] 87, 312 (1913).

⁴ *Ber.*, 45, 899 (1912).

⁵ *J. chim. phys.*, 12, 206 (1914).

⁶ *Ibid.*, 10, 578 (1912).

The author finds another strong objection to the electron conception of valence, perhaps shared by others, in the assumption that all decompositions of molecules are processes of ionization. When one considers the very great difference between the equilibrium in the reaction $\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$, under the influence of heat, and that in the reaction $\text{HCl} \rightleftharpoons \text{H} + \text{Cl}$ as it occurs in aqueous solution, it seems strange to assume that in both cases we have charged hydrogen and chlorine atoms moving about in the neighborhood of each other, under the influence of the same attractive force except for a certain difference in the dielectric constant of the medium.

For any direct evidence as to whether or not atoms of elementary substances are electrically charged during reaction, we must for the present turn to physical investigations of gases. Here, as pointed out by Bates,¹ such evidence as can be found is against the hypothesis. In addition to the opinion expressed by J. J. Thomson we would also note that Le Blanc and Volmer² have recently added to the evidence that in a reacting mixture of hydrogen and chlorine the atoms of these elements are not present in the charged conditions except when under specific ionizing influences.

In conclusion the author would again call attention to the fact that the "electron conception of valence" cannot avoid dealing with the question of chemical affinity, *i. e.*, the attractive force between atoms. It has already developed into a complex mass of hypotheses, both fundamental ones dealing with the existence of electromeric substances, etc., and supplementary ones regarding the electronic formulas of particular substances. Many statements made very categorically are really only hypothetical. It appears to the author quite unjustifiable to go further without explicit statements regarding such questions as the following:

Do atoms which have not gained or lost electrons attract each other? If so, by what means?

What is supposed to be the magnitude of this force existing before the exchange of electrons as compared with that after such an exchange?

What fundamental principle controls this tendency of atoms to gain and lose electrons? That is, what is the fundamental principle on which we are to determine the electronic formulas of substances?

What is the relation, if any, between this tendency and what we usually speak of as the affinity between various atoms?

It could well be said that such questions carry us too far into detail in a field where everything is speculation, if it were not for the fact that assumptions regarding them are involved in every application of the electron conception and that the lack of explicit hypotheses permits inconsistencies to remain concealed too easily. That the whole theory is

¹ *Loc. cit.*

² *Z. Elektrochem.*, 20, 494.

quite hypothetical is quite clear from the fact that there is not a single well established case of the existence of such electrical isomers as we are constantly being asked to assume in great numbers. We must at least ask that the hypotheses involved shall be made very explicit.

Summary.

In the above paper the following objections are raised to the electron conception of valence:

1. The chemical evidence advanced in support of this hypothesis, in as far as it deals with simple phenomena is quite unconvincing.
2. Any application of the theory involves the constant use of assumptions that render it too elastic to be proved or disproved by these applications.
3. The electromeric formulas assigned to chemical compounds are inconsistent with any rule that can be proposed.
4. No single well-established case of electroisomerism is yet known.
5. The evidence of physical experiments is at present opposed to the assumptions on which it is based.
6. The conception necessarily involves assumptions regarding the attractive force between atoms, the attraction of various atoms for electrons, and the relation of this last property to chemical affinity. A number of questions are proposed which should be answered—at least, the hypotheses to be adopted regarding them should be explicitly stated—before the theory is applied to the most perplexing problems of organic chemistry.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

A METHOD FOR THE CALCULATION OF THE HYDRATION OF THE IONS AT INFINITE DILUTION, AND THE IDEAL DIFFUSION COEFFICIENT AS APPLIED TO THE HYDRODIFFUSION OF ELECTROLYTES.

By GEORGE McPHAIL SMITH.

Received February 5, 1915.

Introduction.

If, in the formula for the diffusion coefficient, $dS = -Dq \, dc/dx \, dt$, we regard D as the quantity of the dissolved substance in grams or mols which in unit time, t , passes through the unit distance x in unit cross-section, q , with unit fall of concentration,— c , occurring in this distance, likewise expressed in grams or mols, and if we divide D by M , the molecular weight of the compound in question, then D/M ($= I$, the ideal diffusion coefficient) indicates the quantity of the substance which would pass under the above conditions, provided that each molecule while retaining

its size, configuration, and free-path velocity, had its molecular weight reduced to unity, and, therefore, its momentum reduced to a corresponding degree.¹ By dividing the diffusion coefficients, determined at 20° in aqueous solution for nonelectrolytes, by the respective values of M , and plotting $\log D/M$ against $\log M$, the points so obtained have been found to lie on a straight line not passing through the origin, and whose equation must be, $\log D/M + n \log M = \log K$, where n is the slope of the line, and K proves to have practically the same value for a great variety of substances. By taking the antilog of both sides, a new fundamental law of diffusion, $DM^{n-1} = K$, has been obtained, according to which we can write $M = (K/D)^{1/n-1}$, and determine M for nonelectrolytes for which D has been measured experimentally.²

With the available data concerning the diffusion of the metals in liquid mercury, it has been found possible by means of this law to study the constitution of certain dilute, liquid amalgams, and it has been shown that, at ordinary temperatures, the metals indicated exist in mercurial solution in molecular forms corresponding to the formulas: Zn, Cd, Sn, Pb, AuHg₂, TlHg₂, LiHg₃, NaHg₃, CaHg₃, KHg₃, RbHg₃, SrHg₃, CsHg₃, BaHg₃.³

It is the object of the present paper to show that an analogous method can be applied in the study of the question concerning the hydration of the ions, the ionic mobilities in this case being treated in the same manner as were the diffusion coefficients of the metals in the study of the constitution of the dilute liquid amalgams. Such a method in the case of the ionic mobilities is justified by the following considerations.

Since at each moment, during the passage of electricity through the solution of an electrolyte, the individual (univalent) ions are under the influence of equal forces, the velocities of the individual ions, both positive and negative, are proportional to their equivalent conductances (mobilities). Also, the magnitude of the impelling force, which results from the potential gradient, and which acts upon the ions, is, under like external conditions, equally great for all univalent ions.⁴ And, moreover, the conductance of a solution of a binary electrolyte, in which there is present a

¹ In the original paper (THIS JOURNAL, 36, p. 848, l. 38) the expression "to the reciprocal value" was used. The passage should read: "but the momentum of each such imaginary molecule of unit molecular weight would be equal only to $1/M$ times that of a molecule of the real compound." This correction should also be applied to the definition of the ideal diffusion coefficient given on p. 849, l. 10.

² G. McP. Smith, THIS JOURNAL, 36, 847 (1914).

³ G. McP. Smith, Z. anorg. Chem., 88, 161 (1914); cf. also E. Beckmann and O. Liesche, Ibid., 89, 171 (1914).

⁴ For ions of the valence n the impelling force is, of course, n times as great. But polyvalent ions, owing to their tendency to enter into the formation of intermediate ions and other complexes, which renders uncertain the extrapolated values obtained for their mobilities at infinite dilution, will not be considered in this paper.

given concentration of free univalent ions, is proportional to the sum of the mobilities of the latter; and, since the quantities of electricity transported by the anion and cation are directly proportional to their individual mobilities, it follows that the velocities of the individual ions, and therefore the numbers that pass in unit time through unit distance are proportional to their mobilities.

When an ion of the mass M is subjected to the action of a constant force, F , it receives a certain acceleration, a , such that we have the relationship expressed by the equation, $F = Ma$. At the same time, the ion is retarded in its motion by the resistance which it must overcome in its passage through the liquid. If the force continues to act, the ion finally acquires the limit velocity, c , that can be imparted to it by that force; and this velocity is independent of the mass of the ion, but depends upon the viscosity of the liquid and upon the size and configuration of the ion. After having acquired this limit velocity, the ion continues to move at a constant rate of speed, and the resistance R , which it then encounters is exactly equal to the force F , or, what is the same thing, the positive acceleration which the ion acquires from the force F is exactly equal to the negative acceleration which it receives from the resistance R . If, therefore, a given ion, while retaining its charge, size, and configuration, could have its mass, M , reduced to unity, the force F would still impart to it the limit velocity c , but its positive or negative acceleration would then be equal to $M \times a$.

If, now, the original ion of the mass M and the corresponding ideal ion of unit mass were both traveling at the limit velocity c , and the force F should suddenly cease to act, the resistance R would initially obtain in both cases; the ion of the mass M would meet with an initial negative acceleration equal to a , while the corresponding ideal ion of unit mass would encounter an initial negative acceleration equal to $M \times a$; or, the kinetic energy of the real ion would be equal to $\frac{1}{2}Mc^2$, while that of the imaginary ion would be equal to $\frac{1}{2}c^2$. That is to say, the periods of time, t , in which the forward progress of the two ions would be brought to a standstill, and the distances, s traversed by them, would bear to one another the approximate relationships:

$$t_1 : t_M = s_1 : s_M = \frac{1}{2}c^2 : \frac{1}{2}Mc^2 = c/M : c = l/M : l; \text{ and } s_1 = s_M/M.$$

Now, in the case of diffusion, according to the kinetic theory, the dissolved molecules (and what is said of the molecules applies equally well to the ions present in a salt solution) are incessantly moving about in irregular zig-zag paths, *with continually changing velocities*, and these are dependent not only upon the resistances encountered by the molecules, but also upon the masses of the latter; the mean free-path velocities of the molecules vary inversely as the square roots of their masses. There-

fore, if a molecule of the mass M has the free-path velocity c_M , and if, with its mass reduced to unity, it would have the free-path velocity c_1 , then, according to the kinetic theory, $c_1 = c_M \sqrt{M}$; the kinetic energies E of the respective molecules are $E_M = \frac{1}{2} M c_M^2$, and $E_1 = \frac{1}{2} c_1^2$, and these are equal. But if the corresponding ideal molecule, in addition to having its mass reduced to unity, be supposed also to retain its original free-path velocity c_M , then its kinetic energy $E'_1 = \frac{1}{2} c_M^2$, and this is equal, not to E_M , but to E_M/M . In that case, provided that the real and the ideal molecules make the same number of movements,¹ we should have for the two neutral molecules the relationships:

$$E'_1 : E_M = \frac{1}{2} c_M^2 : \frac{1}{2} M c_M^2 = c_M/M : c_M = s_M/M : s_M = D/M : D,$$

in which D is the diffusion coefficient of the compound in question; or, in the case of a similarly related pair of univalent ions, the relationships:

$$E'_1 : E_M = c_M/M : c_M = s_M/M : s_M = l/M : l,$$

in which l is the mobility of the ion in question.

The values of D/M are the ideal diffusion coefficients of the compounds, and those of l/M are proportional to the ideal diffusion coefficients of the ions in question. It should especially be noted that, in the foregoing discussion, ideal counterparts of the molecules of each separate compound (or ion) are imagined to exist, which, while retaining the exact size, configuration, and free-path velocity of the real molecules and ions, and while performing the same number of movements, differ from them only in that their masses are equal to unity.

Viewed in this light, the values of l/M assume a real physical significance, and we obtain in them a common denominator, to which the mobilities of the different ions might be reduced, if only their absolute hydration (*i. e.*, their ion-weights) were known. Since the l/M values are proportional to the ideal diffusion coefficients of the independent hydrated ions, we should expect in this case also to find the law to hold, that $lM^{n-1} = K$.

A. The Relative Hydration of the Ions.

During the last twenty-five or thirty years, there has been accumulated along various lines a great deal of evidence in favor of the view that the ions are more or less hydrated in aqueous solution.² Among the strongest

¹ After each movement, the ideal molecule is supposed to pause and wait until the real molecule has finished its movement, whereupon they both start out again together, and so on, over and over again.

² Cf. G. Bredig, "Beiträge zur Stöchiometrie der Ionenbeweglichkeit," *Z. physik. Chem.*, **13**, 191-288 (1894); W. R. Bousfield, "Ionengrößen in Beziehung zur Leitfähigkeit von Elektrolyten," *Ibid.*, **53**, 257-313 (1905); E. H. Riesenfeld and B. Reinhold, "Berechnung der Ionenhydratation aus der Überföhrungszahl und der Beweglichkeit," *Ibid.*, **66**, 672-86 (1909); and, especially, E. W. Washburn, "Hydrates in Solution: A Review of Recent Experimental and Theoretical Contributions," *Technology Quarterly*, **21**, 360-449 (1908).

evidence in favor of this view is that which has been deduced from the results of transference experiments which have been carried out with various salt solutions in the presence of different nonelectrolytic reference substances. If at the end of such an experiment the ratio of water to nonelectrolyte has changed at the electrodes, then it follows either that the ions have carried water in the one direction, or that they have carried the nonelectrolyte in the opposite direction. Buchböck,¹ who was the first to obtain satisfactory quantitative results with this method, electrolyzed hydrogen chloride solutions, using mannite or resorcinol, at widely differing concentrations, as the reference substance; and, more recently, Washburn² has electrolyzed sodium chloride solutions with three different reference substances, sucrose, raffinose, and arsenious acid. These experiments all harmonize well together, and, unless we are prepared to assume that all of the different reference substances are capable of combining with the ions in the same way, the conclusion would seem to be justified that the changes in the ratio of water to nonelectrolyte at the electrodes are due, at least in the main, to the transfer of water from one part of the solution to another by the ions.

The relative degrees of hydration of chloride, hydrogen, potassium, sodium, and lithium ions, at 25°, in solutions containing about 1.25 formula weights of the metallic chlorides, and 0.1 formula weight of raffinose, to 1000 g. of water, or 1-1.5 formula weights of hydrogen chloride and up to 0.3 formula weight of mannite to 1000 g. of water, have been determined experimentally by E. W. Washburn,³ according to whom, if we assume that the hydrated chloride ion contains on the average 9 molecules of water, we have for these ions the degrees of hydration which are indicated in the first column of Table I.

TABLE I.

| No. | Hydrated ion. | Mobility, ⁴ l_0 25°. | log l . | M . | log M . | log 10/ M . | $lM^{n-1} = K$. |
|--------|-------------------------------------|--------------------------------------|-----------|-------|-----------|---------------|------------------|
| 1..... | $[\text{H}(\text{OH}_2)_{2.0}]^+$ | 350 | 2.54407 | 37.04 | 1.56867 | 1.97540 | 8773 |
| 2..... | $[\text{Cl}(\text{HOH})_{9.0}]^-$ | 75.8 | 1.87967 | 197.6 | 2.29579 | 0.58388 | 8458 |
| 3..... | $[\text{K}(\text{OH}_2)_{10.8}]^+$ | 74.8 | 1.87390 | 228.3 | 2.35851 | 0.51539 | 9472 |
| 4..... | $[\text{Na}(\text{OH}_2)_{16.8}]^+$ | 51.2 | 1.70927 | 322.1 | 2.50799 | 0.20128 | 8848 |
| 5..... | $[\text{Li}(\text{OH}_2)_{26.3}]^+$ | ... | ... | 462.7 | ... | ... | ... |

Mean, 8888

¹ *Z. physik. Chem.*, **55**, 563 (1906).

² *THIS JOURNAL*, **31**, 322 (1909); *Z. physik. Chem.*, **66**, 513 (1909).

³ *Loc. cit.* The relative hydration of hydrogen and chloride ions are calculated by Washburn from a portion of the experimental data of Buchböck, who does not state the temperature at which he worked. Washburn, himself, did not work with hydrogen chloride solutions.

⁴ The mobilities given in the table are taken from a paper by A. A. Noyes and K. G. Falk, *THIS JOURNAL*, **34**, 479 (1912). The mobility of lithium ion at 25° has never been determined; the approximate value may, however, be calculated by means of the formula: $l_0 25^\circ = K/M^{n-1} = 8888/(462.7)^{0.892} = 37.3$.

If, now, we plot the values of $\log l/M$ against those of $\log M$, we obtain the points shown in Fig. 1, which are seen to lie on the straight line AB . The slope of this line, n , is equal to $140 \div 74 = 1.892$.

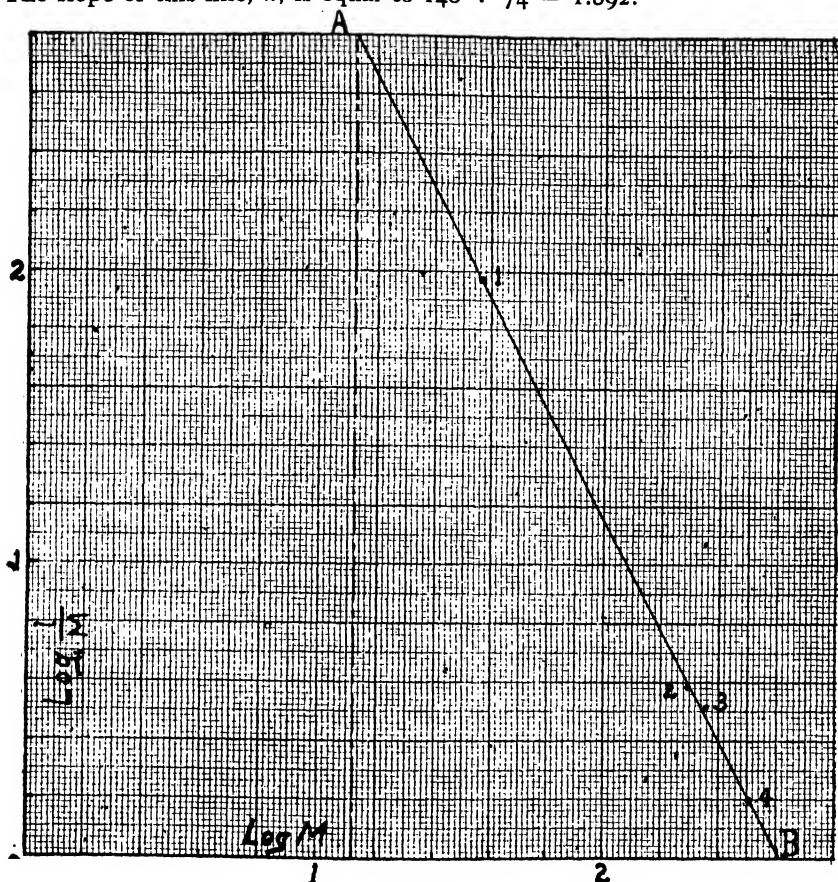
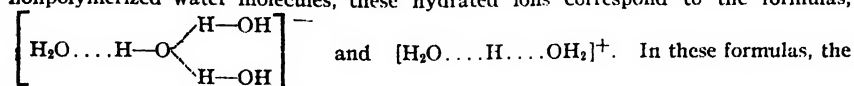


Fig. 1.

On the basis of the assumption that 2 and 3 are the respective maximum coordination numbers of hydrogen and oxygen,¹ and that these ions there-

¹ The maximum coordination number of oxygen, according to Werner ("Neuere Anschauungen a. d. Gebiete d. anorgan. Chemie, ed. 1913, pp. 257-61) is 3, and from this it would seem to be likely that that of hydrogen is 2; upon this basis, assuming nonpolymerized water molecules, these hydrated ions correspond to the formulas,



dashes represent principal valences, and the dotted lines secondary valences. The polymerization of water can be interpreted as a necessary preliminary step in its ionization; e. g., $\text{HOH} + 5\text{H}_2\text{O} \rightleftharpoons [(\text{H}_2\text{O})_2\text{H}][\text{OH}(\text{H}_2\text{O})_3] \rightleftharpoons [(\text{H}_2\text{O})_2\text{H}]^+ + [\text{OH}(\text{H}_2\text{O})_3]^-$.

Interpolation compound.

fore contain at infinite dilution 2 and 3 molecules of water of hydration, the degrees of hydration of the other univalent ions whose mobilities have been determined can be calculated for infinite dilution at 18° , as follows:

For the line AB , in Fig. 1, we have the equation,

$$\log l/M + n \log M = \log K;$$

whence,

$$lM^{(n-1)} = K, \quad (1)$$

and

$$M = (K/l)^{1/n-1}. \quad (2)$$

Assuming that the same law holds at 18° for zero concentration, we have only to substitute in (1) the values of $l_{0, 18^\circ}$, and of M , for the two ions, and we get the relationships:

$$314.5 \times 37.04^{(n-1)} = K = 174 \times 71.05^{(n-1)};$$

whence

$$n = 1.9087,$$

and

$$K = 8378.$$

And, in order to calculate the hydrated-ion weights of the other univalent ions, we then substitute these values in (2):

$$M = (K/l)^{1/n-1} = (8378/l)^{1.1004}.$$

The values thus obtained, together with the numbers of hydrated water molecules, are given in Table II, and, in addition, the last column of the table contains the degrees of hydration calculated by Washburn from the experimental data at 25° , on the assumption that the chloride ion carries 9 molecules of water (cf. Table I).¹

It is very noteworthy that, starting with the data obtained at 25° by means of transference experiments with mixtures containing about 1.25 mols of electrolyte, 0.1 mol of reference substance, and 55.5 mols of water, assuming chloride ion to be combined with 9 molecules of water and taking the resulting experimental values for the other four ions, the law is found to hold, that $l_{0, 25^\circ} \times M^{n-1} = K$; and that, starting with the assumptions that hydrogen and hydroxide ions at infinite dilution, respectively, contain, at 18° , 2 and 3 hydrated molecules of water, and that the law, $l_{0, 18^\circ} \times M^{n-1} = K$, holds in this case, we obtain upon calculation practically identical values for the degrees of hydration of the same ions under these widely differing conditions. This fact furnishes confirmatory evidence that in each of the above mentioned transference experiments with electrolyte and nonelectrolytic reference substance, the changes in ratio between reference substance and water at the elec-

¹ In his paper, Washburn determines the relationship which exists between the degree of hydration of each of the four positive ions and that of chloride ion, and in a table he gives the number of molecules of water which are combined with each of these ions for different assumptions regarding the number combined with the chloride ion. In the present paper, those of Washburn's values are taken which are based upon the assumption that chloride ion is combined with 9 molecules of water; since in that case it results that 2 molecules of water are assigned to the hydrogen ion.

trodes were due almost wholly to the transfer of water, and not to that of reference substance, by the ions.

TABLE II.

| Ion. | Mobility, ¹ l_0 18°. | $\log l$. | $\log M$. | M . | Molecules of hydrated water calculated for zero concen- tration at 18°. | Washburn's corre- sponding values at 25° based on $[\text{Cl}(\text{OH}_2)_6]^-$ for mixtures of 1.25 mols salt and 55.5 mols water. |
|------------------------|--------------------------------------|------------|------------|-------|---|--|
| | | | | | | |
| H..... | 314.5 | ... | ... | 37.04 | 2.0 | 2.0 ± 0.04 |
| OH..... | 174 | ... | ... | 71.05 | 3.0 | .. |
| Cs..... | 68.0 | .83251 | 2.30051 | 200 | 3.7 | [9.9 (E. B. Millard)] ² |
| Br..... | 67.7 | .83059 | 2.30262 | 201 | 6.7 | .. |
| Rb..... | 67.5 | .82930 | 2.30404 | 201 | 6.4 | .. |
| I..... | 66.6 | .82347 | 2.31045 | 204 | 4.3 | .. |
| Tl..... | 65.9 | .81889 | 2.31549 | 207 | 0.15 | .. |
| Cl..... | 65.5 | .81624 | 2.31841 | 208 | 9.6 | 9.00 |
| NH ₄ | 64.7 | .81090 | 2.32426 | 211 | 10.7 | .. |
| K..... | 64.5 | .80956 | 2.32576 | 212 | 9.6 | 10.5 ± 0.2 |
| NO ₃ | 61.8 | .79099 | 2.34619 | 222 | 8.9 | .. |
| SCN..... | 56.7 | .75358 | 2.38736 | 244 | 10.3 | .. |
| ClO ₃ | 55.1 | .74115 | 2.40104 | 252 | 9.3 | .. |
| Ag..... | 54.3 | .73480 | 2.40803 | 256 | 8.2 | .. |
| BrO ₃ | 47.6 | .67761 | 2.47096 | 296 | 9.3 | .. |
| F..... | 46.7 | .66932 | 2.48008 | 302 | 15.7 | .. |
| Na..... | 43.4 | .63749 | 2.51511 | 327 | 16.9 | 16.6 ± 0.2 |
| IO ₃ | 34.0 | 1.53148 | 2.63176 | 428 | 14.1 | .. |
| Li..... | 33.3 | 1.52244 | 2.64171 | 438 | 24.0 | 25.3 ± 0.4 |

It should also be mentioned that Buchböck,³ who worked with solutions containing hydrogen chloride and reference substance at different concentrations, extrapolates his hydration values to zero concentration, both of hydrogen chloride and of the reference substance, and comes to the conclusion that, at infinite dilution, chloride ion is combined with 4 molecules of water for each water molecule that hydrogen ion is combined with; *i. e.*, if hydrogen ion carries 2 water molecules, chloride ion carries 8. This conclusion is in surprising agreement with the calculated value for chloride ion (Table II).

It is further interesting to note that Washburn and MacInnes⁴ have

¹ The mobilities given in the table, with the exception of that of hydroxide ion, are taken from the paper by Noyes and Falk, *Loc. cit.* The value for hydroxide ion is that given in Landolt-Börnstein-Meyerhoffer's Tabellen, 4th ed. (1912), p. 1124; it is less accurately known than the others, and may be 2 or 3% in error, while that for hydrogen ion is less than 1% in error (Private communication from Dr. S. J. Bates). Owing to the lesser accuracy of the determined values of l_0 18° for hydrogen and hydroxide ions, upon which the above table is based, it was not considered worth while in the case of the salts to use the somewhat more accurate values of Bates (THIS JOURNAL, 35, 519 (1913)).

² See below.

³ *Loc. cit.*

⁴ E. W. Washburn and D. A. MacInnes, THIS JOURNAL, 33, 1686 (1911).

drawn the conclusion from their cryoscopic data that, in 0.5 *N* solution potassium chloride is combined with about 9, and lithium chloride with about 18 mols of water more than caesium nitrate is combined with. By means of the data in Table II, we arrive at relationships for 18° and zero concentration which are in as good agreement with these conclusions as could be expected; the figures so obtained are that potassium chloride is combined with 6.6, and lithium chloride with 21.0 mols of water more than caesium nitrate is combined with.¹

In this connection, however, attention should be called to the fact that, by means of transference experiments, at 25°, with caesium chloride solution, with raffinose as the reference substance, E. B. Millard² has recently determined the relative degree of hydration of caesium ion; he concludes from his work that caesium ion carries 0.65 mol of water less than potassium ion does. According to him, if potassium ion combines with 10.5 mols of water, then caesium ion, under the same conditions, combines with 9.9 mols of water. This result is very surprising, when it is viewed in the light of the good agreement obtained in all other cases. Furthermore, additional evidence in favor of the calculated values is furnished in the next section, where it is shown that these values may be used to advantage in connection with the ideal diffusion coefficient and the hydrodiffusion of electrolytes.

B. The Ideal Diffusion Coefficient and the Hydrodiffusion of Electrolytes.

L. W. Öholm³ has determined, at 18° and 0.01 *N* concentration, the diffusion coefficients of the following highly dissociated electrolytes: NaCl, KCl, LiCl, KI, HCl, KOH, and NaOH. At infinite dilution—and the same would hold approximately at 0.01 *N* concentration—the ions of these electrolytes would diffuse independently, if it were not for their electrical charges; but the differences in potential, which result from the tendency of the lighter to precede the heavier ions, tend to hold the faster lighter ones back, while pulling the slower heavier ones forward. The net result, of course, is that the electrolytes diffuse upwards as a whole, virtually in the form of vibrating labile systems, each of which consists of one positive and one negative ion. Therefore, by taking as the molecular weights of the electrolytes the sums of the hydrated-ion weights of their positive and negative ions (Table II), it should be possible to successfully apply the conception of the ideal diffusion coefficient to the question of

¹ Washburn and MacInnes assume in their paper that caesium nitrate is not at all hydrated.

² Thesis submitted to the Graduate Faculty of the University of Illinois in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry, 1914, p. 28.

³ *Z. physik. Chem.*, 50, 309 (1904-05).

the hydrodiffusion of these substances. The data listed in Table III, in which the D_{18° values are those determined experimentally at 0.01 N concentration, show in a convincing manner that this actually can be done.

TABLE III.

| No. | Added formulas of hydrated ions (Table II). | D_{18° | $\log D$ | Sum of hydrated- ion weights. (Table II). | | $\log M$ | $\log 10^3 D/M$ | $DM^{n-1} = K$. |
|--------|---|----------------|----------|---|--|----------|-----------------|------------------|
| | | | | M . | | | | |
| 1..... | HCl.11.6H ₂ O | 2.324 | 0.36624 | 245 | | 2.38917 | 0.977 | 274 |
| 2..... | KOH.12.6H ₂ O | .903 | 0.27944 | 283 | | 2.45179 | 0.828 | 254 |
| 3..... | NaOH.19.9H ₂ O | .432 | 0.15594 | 398 | | 2.59988 | 0.556 | 257 |
| 4..... | KI.13.9H ₂ O | .460 | 0.16435 | 416 | | 2.61909 | 0.545 | 272 |
| 5..... | KCl.19.2H ₂ O | .460 | 0.16435 | 420 | | 2.62325 | 0.540 | 274 |
| 6..... | NaCl.26.5H ₂ O | .170 | 0.06819 | 535 | | 2.72835 | 0.340 | 271 |
| 7..... | LiCl.33.6H ₂ O | .000 | 0.00000 | 646 | | 2.81023 | 0.190 | 273 |

Upon plotting the values of $\log D/M$ against those of $\log M$, the points shown in Fig. 2 are determined, and these are seen to lie upon the straight line AB , whose slope, n is equal to $140 \div 75 = 1.8667$. That is, upon taking into consideration the hydration of the ions, the diffusion of the highly dissociated electrolytes is found to be essentially no more com-

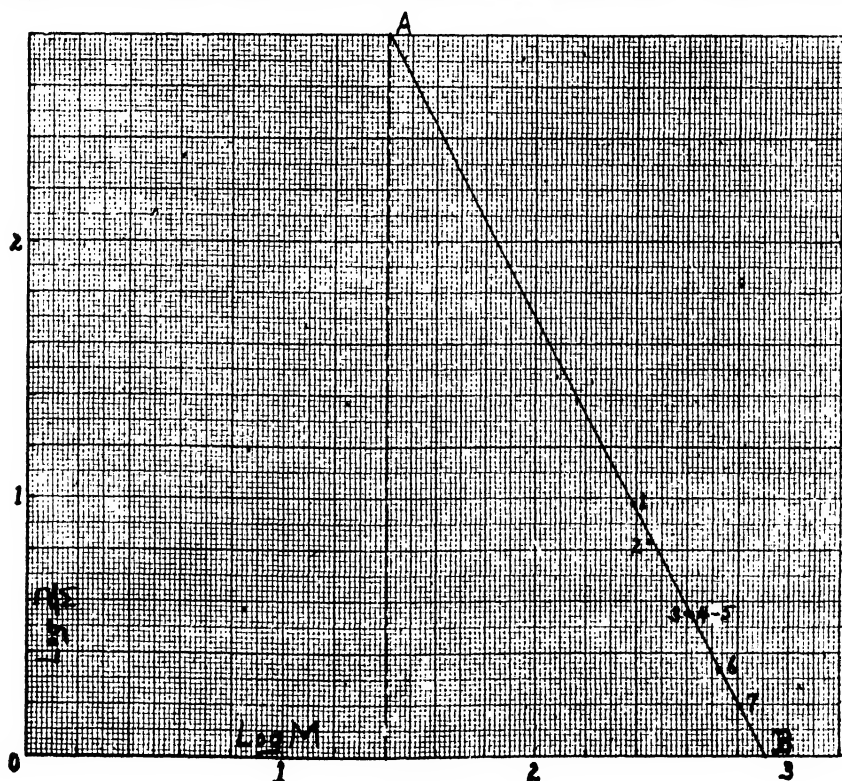


Fig. 2.

plicated than that of the nonelectrolytes; we have in this case also the law, $DM^{n-1} = K$. The values of K , which have been calculated for the different substances, are included in the last column of Table III. Their excellent agreement furnishes evidence which points almost convincingly to the correctness of the data calculated for ionic hydration at infinite dilution.

It will perhaps not be out of place also to note at this point that, by combining the two laws, $DM^{n-1} = K$, and $lM^{n-1} = K$, a diffusion formula can be obtained, which bears a striking resemblance to that developed along entirely different lines by Nernst.

For the diffusion of the hydrated electrolytes, we have

$$D_{18^\circ} M^{0.8667} = 270,$$

or, since $M_{\text{Electrolyte}} = M_{\text{Cation}} + M_{\text{Anion}}$, we have,

$$D_{18^\circ} = 270 / (M_K + M_A)^{0.8667}. \quad (3)$$

In the case of the hydrated ions, we have,

$$M_K = (K/l_K)^{1/n-1} \quad \text{and} \quad M_A = (K/l_A)^{1/n-1};$$

or,

$$M_K = (8378/l_K)^{1.1004} \quad \text{and} \quad M_A = (8378/l_A)^{1.1004}.$$

Substituting in (3) these values of M_K and M_A , we obtain,

$$D_{18^\circ} = \frac{270}{[(8378/l_K)^{1.1004} + (8378/l_A)^{1.1004}]^{0.8667}} = 0.04896 \left(\frac{l_K^{1.1004} \cdot l_A^{1.1004}}{l_K^{1.1004} + l_A^{1.1004}} \right)^{0.8667}. \quad (4)$$

According to Nernst,¹ on the other hand, $D_{18^\circ} = 0.04485 \left(\frac{l_K \cdot l_A}{l_K + l_A} \right)$

This formula furnishes values for infinite dilution.

By means of the formula, $D = K/M^{n-1} = 270 / (M_K + M_A)^{0.867}$, it is of course possible to calculate the diffusion coefficients of other uni-univalent electrolytes, for 18°, at 0.01 *N* concentration. For nitric acid and sodium iodide, for example, we obtain the values 2.18 (2.13, at 0.13 *N*) and 1.17 (1.115, at 0.086 *N*).²

In conclusion, a summarized list of the cases in which the law, $DM^{n-1} = K$, has been found to hold, together with the corresponding values of n and K , is given in Table IV:

¹ Theoretische Chemie, 5th ed. (1907), p. 371, Equation 8. For the diffusion coefficients of hydrogen chloride and sodium hydroxide, we obtain by means of Nernst's formula the values, 2.431 and 1.558; the writer's Formula 4, gives 2.294 and 1.505; Öholm's values are 2.324 and 1.432.

² The values in parenthesis are given by Öholm (*Loc. cit.*, p. 333), who obtains them by recalculation to 18° of Scheffer's value for nitric acid, and of Kawalki's value for sodium iodide.

TABLE IV.

| Case. | Concentration. | Temperature. | η . | K . |
|--|----------------|--------------|----------|-------|
| Hydrodiffusion of nonelectrolytic organic compounds..... | 0.25 | 20° | 1.505 | 7.00 |
| Hydrodiffusion of nonelectrolytic organic compounds..... | zero | 20° | 1.489 | 6.66 |
| Hydrodiffusion of nonelectrolytic organic compounds ¹ | 0.25 | 10 \pm 1° | 1.489 | 4.77 |
| Hydrodiffusion of gases..... | very low | 18 \pm 2° | 1.533 | 10.0 |
| Diffusion of metals and metallic compounds in mercury..... | very low | 10 \pm 2° | 1.458 | 13.9 |
| Hydrodiffusion of highly ionized (hydrated) electrolytes..... | 0.01 | 18° | 1.867 | 270 |
| Independent diffusion of hydrated univalent ions ($LM^{n-1} = K$)..... | zero | 18° | 1.909 | 8378 |

URBANA, ILL.

[COMMUNICATION FROM THE CHEMICAL LABORATORY OF PRESIDENCY COLLEGE.]

THE INFLUENCE OF AN ALTERNATING CURRENT ON ELECTROLYSIS BY A DIRECT CURRENT.

[PART II.]

BY JNANENDRA CHANDRA GHOSH.

Received January 26, 1915.

In a previous communication² the action of an alternating current of high frequency on simple voltaic cells was studied. In this communication the influence of an alternating current on electrolytic cells will be described.

Löb³ investigated the solution of metals in potassium cyanide solution under the influence of unsymmetrical alternating currents. Von Wartenburg and Archibald⁴ investigated the formation of ozone at the anode in sulfuric acid solution by means of an alternating current impressed on a direct current. The object of this investigation, however, is to determine how an alternating current affects the phenomenon of electrolysis in general.

The poles of a four-volt lead accumulator were connected through the secondary circuit of an induction coil, and a suitable resistance, to the two electrodes of a voltmeter. The induction coil used was a small one,

¹ In the former paper, the values given for this case are erroneous. Only a portion of Öholm's data was available at that time, and upon taking into consideration also his later work at 10°, the values given in this table are found to be correct (cf. L. W. Öholm, *Z. physik. Chem.*, **70**, 393ff. (1910); *Medd. k. Vetenskapskad. Nobelinst.*, Vol. **2**, No. 23 (1913)).

² *THIS JOURNAL*, **36**, 2333 (1914).

³ *Z. Elektrochem.*, **12**, 79 (1906).

⁴ *Ibid.*, **17**, 812 (1911).

as is generally used in the measurement of conductivity by the Kohlrausch method, and had a frequency of about thirty thousand per min. The amount of electrolytic decomposition in a given amount of time was estimated—firstly when there was an alternating current in the circuit and secondly, when there was no such current.

Electrolysis in Reversible Cells.—The silver voltameter was the first cell to be studied. Care was always taken that the voltameter in the two cases should be identical; otherwise, there is the possibility of the resistance of the circuit being different in the two cases, thus vitiating the accuracy of the results. This was secured by using the same platinum crucible, by filling it up with the silver nitrate solution to the same height, and by using identical silver anodes.

No. 1. (a) Weight of silver when there were both the direct and the alternating current in the circuit, 0.2451 g. in two hours.

(b) Weight of silver when the direct current was flowing through the above circuit for two hours, 0.2415 g.

No. 2. (a) Weight of silver, 0.2873 g.

(b) Weight of silver, 0.2904 g.

It will be seen that there is practically no difference in the amount of electrolytic decomposition in the two cases. We have already seen that, when an alternating current is passed through a reversible voltaic cell, there is no change in the electrode potentials of the cell. A reversible electrolytic cell remains likewise unaffected by an alternating current.

Electrolysis in Irreversible Cells.—In this type of cells it is rather difficult to get correct results. The back electromotive force of polarization becomes constant when the current has passed through the circuit for a considerable time; furthermore, the gases evolved are somewhat soluble in water. These sources of error could be partially eliminated by making the measurements after the current has already passed through the circuit quite a long while. In all the experiments the source of the current was a four-volt battery of two lead accumulators and the current passing through the primary of the induction coil was 0.33 ampere. The external metallic resistance was always kept constant. The results obtained are given in the following tables.

It will be seen that in most of the cases studied, a greater amount of current flows through the circuit during the passage of an alternating current. The exceptions are No. 4 in Table I, No. 5 in Table II, and No. 5 in Table IV. In these exceptional cases the cathodes used were of Pt black, copper or iron. It will also be observed that the smaller the area of the electrodes, the greater is the actual difference between the amount of current in the two cases. In the electrolysis of acids the alternating current is specially efficacious in the case of the cell where mercury is the cathode.

TABLE I.—ELECTROLYTE 0.5 M H₂SO₄.

| Cathode. | | | Anode. | | Cc. H ₂ in 30 min. | |
|----------|--------|---------|--------|---------|-------------------------------|----------|
| | Metal. | Sq. cm. | Metal. | Sq. cm. | DC. | DC + AC. |
| 1..... | Pt | 8.5 | Pt | 8.5 | 7.00 | 7.95 |
| 2..... | Pt | 1.5 | Pt | 1.5 | 6.70 | 8.60 |
| 3..... | Pt | 8.5 | Pt bl. | large | 8.50 | 8.90 |
| 4..... | Pt bl. | large | Pt | 8.5 | 9.50 | 9.60 |
| 5..... | Hg | 3 | Pt | 8.5 | 4.20 | 6.30 |
| 6..... | Hg | 3 | Pt bl. | large | 6.50 | 8.00 |

TABLE II.—ELECTROLYTE 0.1 M H₂C₂O₄.

| | | | | | | |
|--------|--------|-------|----|-----|------|------|
| 1..... | Pt | 8.5 | Pt | 8.5 | 5.60 | 6.70 |
| 2..... | Pt | 1.5 | Pt | 1.5 | 3.40 | 4.65 |
| 3..... | Hg | 3.0 | Pt | 8.5 | 3.40 | 4.90 |
| 4..... | Hg | 7.5 | Pt | 3.0 | 2.84 | 5.40 |
| 5..... | Pt bl. | large | Pt | 2.0 | 7.40 | 7.50 |

TABLE III.—ELECTROLYTE 0.1 M NaOH.

| | | | | | | |
|--------|--------|-----|----|-----|------|------|
| 1..... | Pt bl. | 8 | Pt | 1.5 | 3.90 | 4.30 |
| 2..... | Pt | 1.5 | Pt | 1.5 | 3.10 | 4.05 |
| 3..... | Cu | 3 | Pt | 1.5 | 2.95 | 4.10 |
| 4..... | Sn | 3 | Pt | 1.5 | 2.10 | 3.30 |
| 5..... | Fe | ... | Pt | 1.5 | 4.80 | 5.80 |

TABLE IV.—ELECTROLYTE 0.5 M Na₂SO₄.

| | | | | | | |
|--------|----|-----|--------|-------|------|------|
| 1..... | Pt | 8.5 | Pt | 8.5 | 3.50 | 4.10 |
| 2..... | Pt | 1.5 | Pt | 1.5 | 2.55 | 4.20 |
| 3..... | Pt | 3.5 | Pt bl. | large | 4.10 | 4.50 |
| 4..... | Cu | 3.0 | Pt | 3.0 | 3.30 | 3.40 |
| 5..... | Fe | ... | Pt | 3.0 | 2.20 | 2.10 |

Alternating Current of Itself Ineffective to Bring about Visible Decomposition.

It might be supposed that the alternating current of itself forms the electrolytic gas, as had been observed by Van Name and Grafenberg¹ who used an alternating current having a frequency of 6600 per minute. Experiments were therefore performed to determine whether an alternating current from a small induction coil having a frequency of 30000 per minute could produce any perceptible amount of gas. The results obtained were always in the negative. This result is quite in accord with the observation of LeBlanc² that the action of alternating current diminishes regularly as the number of alternations per minute increases. Besides the strength of the alternating current is too small. The increase in the amount of electrolysis, when there is an alternating current in the circuit, is therefore not due to the electrolysis caused by the alternating current of itself.

¹ *Z. Elektrochem.*, 10, 303^f (1904).

² *Ibid.*, 11, 705 (1905).

The only assumption that could reasonably be made as to the cause of this great increase in the amount of current, when an alternating current plays in the circuit, was that the alternating current in some way decreased the back electromotive force set up in the cell. We may refer in this connection to the work of K. Bennewitz¹ who noticed that when electromagnetic waves were allowed to pass through an electrolytic cell, the decomposition potential sank to 1.24, the theoretical value for the oxy-hydrogen cell.

Experimental Method.—The experiment to determine how the discharge potentials of ions are affected by an alternating current, was arranged in the following way:

A is a battery from which a current of variable voltage passed through the electrolytic cell C. Between the battery and the cell are interposed a milliammeter and the secondary of the induction coil. An alternating current is developed in the secondary by passing a current of 0.33 ampere through the primary and the milliammeter is read when the current

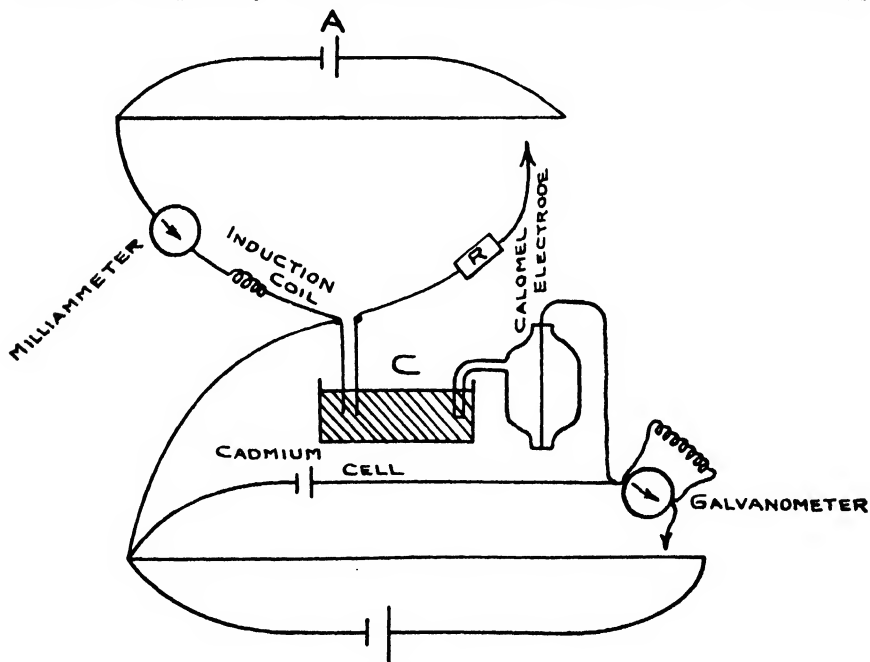


FIG. 1.

passing through the circuit has become constant. In this connection, it may be remarked that the milliammeter remains absolutely steady during the passage of the alternating current. That the milliammeter also records the exact current strength during the passage of the alternating

¹ *Z. physik. Chem.*, 72, 223 (1910)

current was tested by interposing a silver voltameter in the circuit and comparing the readings of the ammeter with the weight of silver obtained. The E. M. F. at each electrode of the electrolytic cell against a decinormal calomel electrode is then measured by means of the potentiometer. The alternating current is now stopped, the milliammeter again read, and the new electrode potentials of the electrolytic cell measured.

The diminution in discharge potential completely accounts for the increase in current strength on the passage of the alternating current. The results obtained with some of the typical electrolytes are given in the following tables. The remarkable drop in the value of the discharge potential will be at once evident. Now, the strength of the current $C = (E - E')/R$, where E is the voltage of the electrolytic current, E' the back electromotive force of polarization. It was always found, that the diminution in the value of E' on the passage of the alternating current completely accounted for the increase in current strength.

TABLE V.

Electrodes of Pt 8.5 sq. cm., each dipped in 0.5 M H_2SO_4 .

| | Strength of current. Amp. | | E. P. at cathode. Volt. | | E. P. at anode. Volts. | |
|--------|------------------------------|----------|----------------------------|----------|---------------------------|----------|
| | DC. | DC + AC. | DC. | DC + AC. | DC. | DC + AC. |
| 1..... | 0.0336 | 0.0375 | -0.820 | -0.660 | +1.650 | +1.630 |
| 2..... | 0.0242 | 0.0275 | -0.790 | -0.610 | +1.600 | +1.600 |
| 3..... | 0.0170 | 0.0210 | -0.745 | -0.570 | +1.580 | +1.580 |
| 4..... | 0.0095 | 0.0110 | -0.580 | -0.530 | +1.530 | +1.530 |
| 5..... | 0.0040 | 0.0052 | -0.530 | -0.490 | +1.510 | +1.510 |
| 6..... | 0.0012 | 0.0020 | -0.290 | -0.280 | +1.440 | +1.445 |

TABLE VI.

Cell consists of Pt 1.5 sq. cm., each dipped in 0.5 M H_2SO_4 .

| | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|
| 1..... | 0.0330 | 0.0400 | -0.910 | -0.630 | +1.680 | +1.650 |
| 2..... | 0.0228 | 0.0300 | -0.850 | -0.590 | +1.630 | +1.590 |
| 3..... | 0.0160 | 0.0230 | -0.810 | -0.550 | +1.620 | +1.590 |
| 4..... | 0.0060 | 0.0121 | -0.770 | -0.520 | +1.550 | +1.550 |
| 5..... | 0.0028 | 0.0040 | -0.505 | -0.500 | +1.490 | +1.480 |

The E. P. of the calomel electrode is taken as zero.

The current strength is altered by varying the voltage of the electrolytic current. The current potential curve is given in Fig. 2.

The electrode potentials at the cathode appear very great but they are in fair accord with those obtained by Newbury¹ with his commutator short-circuited. The diminution in the cathode discharge potential when the alternating current passes through the circuit simultaneously with the direct current, is far greater than the diminution in the anode discharge potential. The effect of decreasing the size of the electrodes could be easily seen by comparing the values recorded in Tables V and VI.

¹ *J. Chem. Soc.*, 14, 19 (1914).

In Expt. 1, Table VI, the cathode discharge potential falls from 0.91 to 0.63 whereas in Expt. 1, Table V, the cathode discharge potential diminishes from 0.82 to 0.66 volt. The anode potential is also much more affected when the area of the electrodes is made smaller. In the current potential curves it will be noticed that in the case where simply a direct current

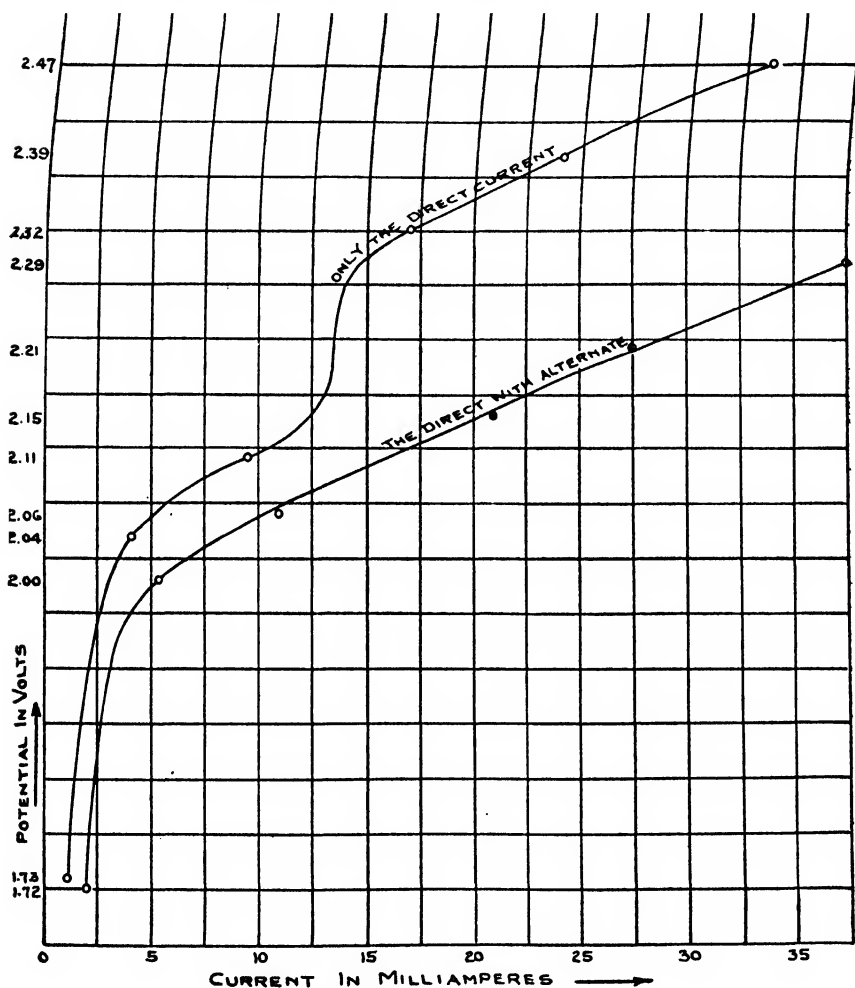


FIG. 2.

passes there is a sharp break at about 2.30 volt. This break is entirely absent when the alternating current passes simultaneously with the direct current. There is also another break in the current potential curve at about 1.95 volt. This latter break, however, occurs at a slightly lower potential when there is a simultaneous alternate current in the circuit.

Now these breaks are attributed by Nernst,¹ Glaser,² Bose,³ to be due to a new variety of ions getting discharged at these points. It therefore follows that whenever such a break disappears on the passage of an alternating current, the liberation of these new ions has been somehow prevented.

The next cells to be studied had mercury as the cathode.

TABLE VII.

Hg as cathode (3 sq. cm.) and Pt as anode (8.5 sq. cm.), electrolyte 0.5 *M* H₂SO₄.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|----------|-----------------------------|----------|---------------------------|----------|
| | DC. | DC + AC. | DC. | DC + AC. | DC. | DC + AC. |
| 1..... | 0.0210 | 0.0300 | -1.535 | -1.140 | +1.600 | +1.640 |
| 2..... | 0.0095 | 0.0180 | -1.490 | -1.040 | +1.540 | +1.63 |
| 3..... | 0.0040 | 0.0120 | -1.360 | -0.980 | +1.400 | +1.530 |
| 4..... | 0.0010 | 0.0050 | -1.110 | -0.820 | +1.370 | +1.500 |
| 5..... | 0.0005 | 0.0025 | -0.820 | -0.660 | +1.360 | +1.480 |

The effect of the alternating current in this cell is very great. The alternating current affects chiefly the cathode when there is a large drop in potential. It will be noticed that the anode potential increases during the passage of the alternating current. This is due to the greater amount of current passing through the circuit in consequence of the large drop in potential at the cathode, and the inability of the alternating current to exert its depolarizing action on the anode. It will also be noticed that the increase in the anode discharge potential becomes very prominent at the back E. M. F. values lower than 2.65 volt, where there is a break in the current potential curve. This value is in agreement with the data given by Caspari⁴ for the E. M. F. required to produce visible decomposition. It is, however, very peculiar that this break disappears when an alternating current passes simultaneously with the direct current through the circuit. In this case, the break appears at a much lower voltage, about 2.2 volt. The current potential curve is given in Fig. 3.

TABLE VIII.

Hg cathode (3 sq. cm.) and large Pt black anode.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|----------|-----------------------------|----------|---------------------------|----------|
| | DC. | DC + AC. | DC. | DC + AC. | DC. | DC + AC. |
| 1..... | 0.0310 | 0.0385 | -1.550 | -1.230 | +1.325 | +1.350 |
| 2..... | 0.0154 | 0.0231 | -1.490 | -1.130 | +1.220 | +1.250 |
| 3..... | 0.0080 | 0.0160 | -1.410 | -1.060 | +1.220 | +1.250 |
| 4..... | 0.0030 | 0.0130 | -1.375 | -1.000 | +1.200 | +1.230 |
| 5..... | 0.0010 | 0.0050 | -1.200 | -0.880 | +1.060 | +1.200 |

¹ *Ber.*, 30, 1547 (1897).

² *Z. Elektrochem.*, 4, 355-73-97, etc. (1898).

³ *Ibid.*, 5, 153 (1868).

⁴ *Z. physik. Chem.*, 30, 89-97 (1899).

It was thought interesting to determine whether by substituting a large foil of Pt black for the platinum anode of the previous cell, the increase in the anode discharge potential observed, during the passage of the alter-

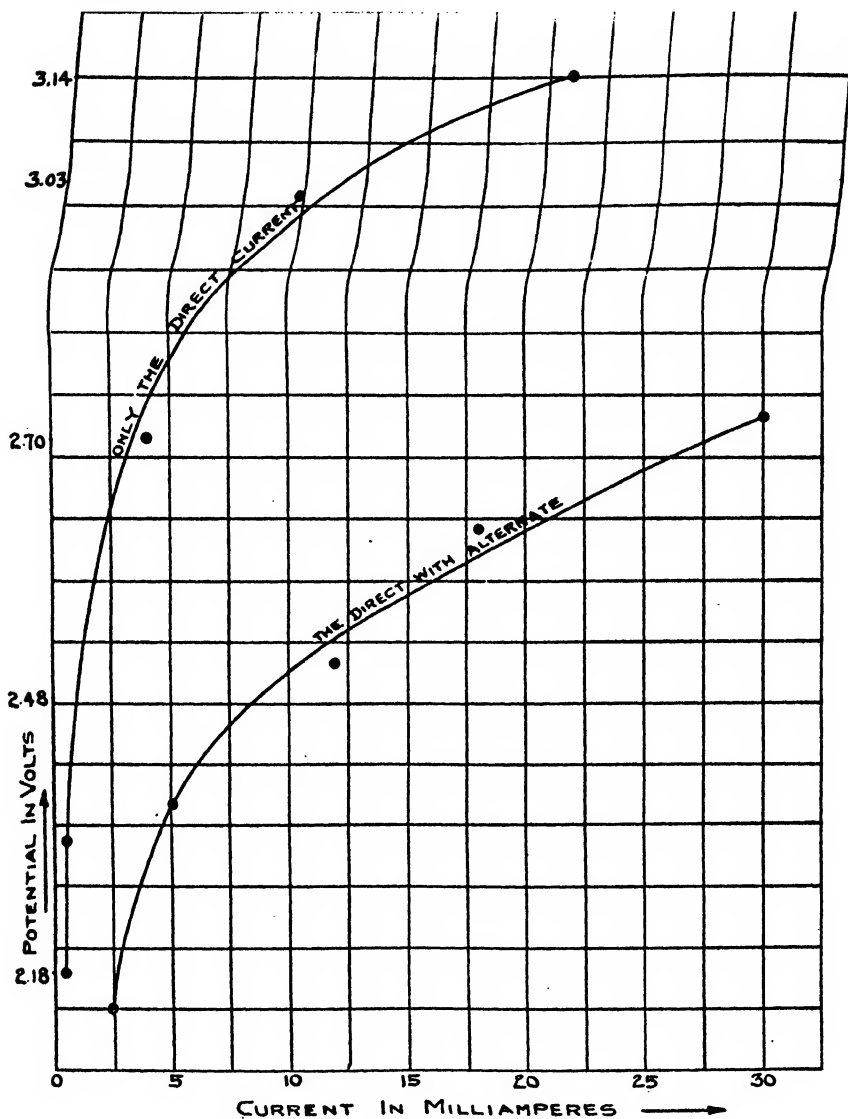


FIG. 3.

nating current, could be eliminated. The results as recorded in Table VIII show, that the increase in potential, even in this case is quite large.

Here too it will be noticed that a break in the current potential curve

occurs at about 2.4 volt. This break disappears on the passage of the alternating current and a break at a much lower voltage occurs instead.

If the sulfuric acid solution in the above cell be substituted by any other acid solution, fairly analogous results are generally obtained. In Tables IX and X are given results obtained with oxalic acid.

TABLE IX.

Pt electrodes (area 8.5 sq. cm.) dipped in 0.1 *N* oxalic acid.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0275 | 0.0320 | -1.157 | -1.000 | +1.700 | +1.670 |
| 2..... | 0.0195 | 0.0222 | -1.010 | -0.910 | +1.590 | +1.590 |
| 3..... | 0.0145 | 0.0170 | -0.965 | -0.850 | +1.550 | +1.550 |
| 4..... | 0.0121 | 0.0150 | -0.930 | -0.820 | +1.520 | +1.520 |
| 5..... | 0.0090 | 0.0110 | -0.890 | -0.770 | +1.350 | +1.405 |
| 6..... | 0.0065 | 0.0080 | -0.830 | -0.720 | +1.210 | +1.275 |
| 7..... | 0.0055 | 0.0070 | -0.818 | -0.700 | +0.940 | +0.995 |
| 8..... | 0.0030 | 0.0045 | -0.760 | -0.650 | +0.770 | +0.815 |
| 9..... | 0.0020 | 0.0030 | -0.690 | -0.600 | +0.675 | +0.720 |

Breaks in the direct current potential curves occur at about 2.65 and at about 2.2. The first break disappears on the passage of the alternating current. The break at 2.2 was noticed by Bose¹ and was supposed to be due to the discharge of COOH' ions. Below the voltage indicated by the second break, the anode potential increases markedly during the passage of the alternating current.

TABLE X.

Hg cathode (3 sq. cm.) and Pt anode (5 sq. cm.) electrolyte 0.1 *N* oxalic acid.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0168 | 0.0028 | -1.615 | -1.274 | +1.750 | +1.830 |
| 2..... | 0.0092 | 0.0160 | -1.520 | -1.106 | +1.510 | +1.680 |
| 3..... | 0.0068 | 0.0130 | -1.470 | -1.040 | +1.480 | +1.640 |
| 4..... | 0.0045 | 0.0100 | -1.430 | -0.940 | +1.400 | +1.590 |
| 5..... | 0.0032 | 0.0078 | -1.385 | -0.850 | +1.210 | +1.480 |
| 6..... | 0.0018 | 0.0060 | -1.330 | -0.780 | +1.000 | +1.310 |

The results are quite analogous to those recorded in Table VII.

The behavior of the normal salts are quite different from that of the acids. The diminution in the cathode discharge potential, on the passage of an alternating current, which is so marked in the case of acids, is not so very prominent here, unless the size of the electrodes be made very small. The results are recorded in Tables XI, XII, XIII, XIV and XV.

¹ *Loc. cit.*

TABLE XI.

Pt electrodes (8.5 sq. cm.) dipped into 0.5 M Na₂SO₄.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0170 | 0.0195 | -1.770 | -1.691 | +1.612 | +1.600 |
| 2..... | 0.0085 | 0.0085 | -1.681 | -1.610 | +1.520 | +1.493 |
| 3..... | 0.0030 | 0.0040 | -1.532 | -1.490 | +1.420 | +1.410 |

TABLE XII.

Same as the preceding but area of electrodes 1 sq. cm.

| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
|--------|--------|--------|--------|--------|--------|---------|
| 1..... | 0.0120 | 0.0200 | -1.970 | -1.670 | +1.615 | +1.610 |
| 2..... | 0.0065 | 0.0128 | -1.875 | -1.590 | +1.540 | +1.520 |
| 3..... | 0.0040 | 0.0098 | -1.680 | -1.530 | +1.520 | +1.510. |
| 4..... | 0.0023 | 0.0055 | -1.631 | -1.510 | +1.490 | +1.465 |
| 5..... | 0.0020 | 0.0036 | -1.403 | -1.350 | +1.480 | +1.450 |
| 6..... | 0.0018 | 0.0020 | -1.070 | -1.130 | +1.440 | +1.355 |
| 7..... | 0.0016 | 0.0016 | -0.900 | -1.020 | +1.435 | +1.330 |

The alternating current decreases the discharge potential both at the cathode and at the anode, the effect on the cathode is more prominent. Experiments No. 6 and 7 in Table XII are peculiar in so far as the cathode discharge potential increases by the action of the alternating current. There is a break in the current potential curve at about 3.2 which disappears on the passage of the alternating current.

By substituting Pt black for the Pt anode, the effect of the alternating current becomes perceptibly less, as is shown in Table XIII, while if Pt black is used as cathode the influence of the alternating current becomes almost negligible.

TABLE XIII.

Pt cathode (3.5 sq. cm.) and large Pt black anode electrolyte 0.5 M Na₂SO₄.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0195 | 0.0210 | -1.911 | -1.842 | +1.285 | +1.292 |
| 2..... | 0.0120 | 0.0135 | -1.890 | -1.823 | +1.250 | +1.265 |
| 3..... | 0.0084 | 0.0097 | -1.851 | -1.770 | +1.230 | +1.240 |
| 4..... | 0.0056 | 0.0071 | -1.770 | -1.690 | +1.211 | +1.225 |
| 5..... | 0.0040 | 0.0050 | -1.670 | -1.620 | +1.951 | +1.200 |
| 6..... | 0.0028 | 0.003 | -1.490 | -1.470 | +1.150 | +1.155 |

TABLE XIV.

Cell consists of Pt electrodes 2.5 sq. cm. each in 0.5 M (COOK)₂ solution.

| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
|--------|--------|--------|--------|--------|--------|--------|
| 1..... | 0.0290 | 0.0342 | -1.761 | .580 | +1.004 | +0.964 |
| 2..... | 0.0205 | 0.0270 | -1.690 | .530 | +0.937 | +0.877 |
| 3..... | 0.0160 | 0.0214 | -1.643 | .490 | +0.917 | +0.857 |
| 4..... | 0.0115 | 0.0161 | -1.602 | .447 | +0.905 | +0.855 |
| 5..... | 0.0075 | 0.0115 | -1.530 | .390 | +0.887 | +0.830 |
| 6..... | 0.0045 | 0.0075 | -1.421 | .318 | +0.835 | +0.800 |
| 7..... | 0.003 | 0.0045 | -1.290 | .252 | +0.810 | +0.795 |
| 8..... | 0.0028 | 0.003 | -1.121 | .150 | +0.570 | +0.610 |

The behavior of potassium oxalate solution is quite analogous to that of sodium sulfate solution. The results are recorded in Tables XIV and XV.

TABLE XV.
Pt cathode (1.5 sq. cm.) large Pt black anode.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0320 | 0.0349 | -1.804 | -1.700 | +0.872 | +0.880 |
| 2..... | 0.245 | 0.0265 | -1.750 | -1.641 | +0.840 | +0.848 |
| 3..... | 0.205 | 0.0224 | -1.710 | -1.610 | +0.830 | +0.840 |
| 4..... | 0.0165 | 0.0185 | -1.682 | -1.581 | +0.825 | +0.832 |
| 5..... | 0.0135 | 0.0155 | -1.640 | -1.551 | +0.810 | +0.818 |
| 6..... | 0.0082 | 0.0102 | -1.580 | -1.495 | +0.780 | +0.790 |
| 7..... | 0.0062 | 0.0080 | -1.535 | -1.440 | +0.780 | +0.785 |
| 8..... | 0.0040 | 0.0060 | -1.465 | -1.380 | +0.750 | +0.750 |
| 9..... | 0.0025 | 0.0033 | -1.375 | -1.340 | +0.700 | +0.710 |

By substituting Pt black for the Pt anode, there is not much change of the alternating current. Also the influence of the alternating current on electrolysis becomes perceptibly smaller. If, however, Pt black be used as cathode, the change in the discharge potential values on the passage of the alternating current becomes almost negligible.

The behavior of an oxidizing salt like potassium nitrate affords many points of interest. The results are recorded in Tables XVI, XVII, XVIII, XIX.

TABLE XVI.
Pt electrodes (8.5 sq. cm.) dipped in 0.5 M KNO₃ sol.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0190 | 0.0230 | -1.610 | -1.460 | +1.710 | +1.680 |
| 2..... | 0.0135 | 0.0166 | -1.550 | -1.400 | +1.655 | +1.640 |
| 3..... | 0.0100 | 0.0138 | -1.535 | -1.385 | +1.630 | +1.615 |
| 4..... | 0.0065 | 0.0097 | -1.480 | -1.365 | +1.595 | +1.575 |
| 5..... | 0.0046 | 0.0065 | -1.335 | -1.270 | +1.570 | +1.555 |
| 6..... | 0.0038 | 0.0040 | -1.080 | -1.090 | +1.550 | +1.530 |
| 7..... | 0.0030 | 0.0030 | -0.850 | -0.880 | +1.540 | +1.510 |

TABLE XVII.
Area of the electrodes 1.85 sq. cm. otherwise as preceding.

| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
|---------|--------|--------|--------|--------|--------|--------|
| 1..... | 0.0140 | 0.0240 | .765 | -1.400 | +1.780 | +1.720 |
| 2..... | 0.0075 | 0.0165 | .660 | -1.316 | +1.750 | +1.660 |
| 3..... | 0.0057 | 0.0150 | .640 | -1.270 | +1.718 | +1.650 |
| 4..... | 0.0036 | 0.0115 | .520 | -1.180 | +1.650 | +1.600 |
| 5..... | 0.0032 | 0.1000 | .376 | -1.188 | +1.680 | +1.600 |
| 6..... | 0.0030 | 0.0070 | .092 | -0.960 | +1.640 | +1.580 |
| 7..... | 0.0023 | 0.0055 | -0.940 | -0.868 | +1.620 | +1.545 |
| 8..... | 0.0020 | 0.0040 | -0.832 | -0.792 | +1.584 | +1.508 |
| 9..... | 0.0016 | 0.0030 | -0.680 | -0.730 | +1.568 | +1.480 |
| 10..... | 0.0015 | 0.0020 | -0.560 | -0.660 | +1.530 | +1.410 |

The peculiarity with potassium nitrate solution is that the anode discharge potential always diminishes on the passage of the alternating current, while the cathode discharge potential increases under conditions of very low current density. The results of Table XVI appear magnified, as it were, in Table XVII, where the area of the electrodes is much smaller. But the break in the direct current potential curves occurs in both cases at about 3 volts. This break, however, is not noticeable when the alternating current passes through the circuit simultaneously with the direct current. We have seen before that the break at 3.0 volts in the current potential curve when the electrolyte is sodium sulfate disappears on the passage of the alternating current. These breaks at such high potentials probably indicate the discharge of the ions of the alkali metals. This discharge perhaps does not take place when the alternating current passes.

TABLE XVIII.

Large Pt black cathode, an anode of Pt (2.5 sq. cm.) dipped into 0.5 *M* KNO₃.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0295 | 0.0325 | -1.096 | -1.100 | +1.880 | +1.750 |
| 2..... | 0.0190 | 0.0220 | -1.088 | -1.090 | +1.788 | +1.630 |
| 3..... | 0.0157 | 0.0190 | -1.086 | -1.086 | +1.770 | +1.620 |
| 4..... | 0.0120 | 0.0150 | -1.070 | -1.070 | +1.756 | +1.610 |
| 5..... | 0.0082 | 0.0115 | -0.810 | -0.850 | +1.710 | +1.560 |
| 6..... | 0.0065 | 0.0090 | -0.664 | -0.744 | +1.690 | +1.540 |
| 7..... | 0.0055 | 0.0080 | -0.590 | -0.672 | +1.675 | +1.530 |
| 8..... | 0.0036 | 0.0055 | -0.520 | -0.588 | +1.640 | +1.500 |

TABLE XIX.

The same as preceding, electrodes reversed.

| | | | | | | |
|--------|--------|--------|--------|--------|--------|--------|
| 1..... | 0.0223 | 0.0300 | -1.848 | -1.480 | +1.310 | +1.320 |
| 2..... | 0.0155 | 0.0230 | -1.768 | -1.390 | +1.265 | +1.300 |
| 3..... | 0.0128 | 0.0206 | -1.740 | -1.340 | +1.265 | +1.290 |
| 4..... | 0.0096 | 0.0172 | -1.700 | -1.290 | +1.240 | +1.280 |
| 5..... | 0.0062 | 0.0140 | -1.640 | -1.220 | +1.200 | +1.268 |
| 6..... | 0.0040 | 0.0100 | -1.565 | -1.140 | +1.100 | +1.230 |
| 7..... | 0.0035 | 0.0070 | -1.510 | -1.100 | +0.880 | +1.170 |
| 8..... | 0.0030 | 0.0050 | -1.510 | -1.020 | +0.740 | +1.120 |

We have seen that by using a Pt black cathode, in the case of the electrolytes studied previously, the effect of the alternating current on electrolysis becomes negligible. But with potassium nitrate solution, such is not the case as is shown by the data in Table XVIII. The influence of alternating current is much greater when Pt black is the anode than when it is the cathode. In the former case, the anodic discharge potential increases on the passage of the alternating current, while the cathodic discharge potential decreases. There is a break in the current

potential curve at about 2.8 and it is at voltages below this break that the increase in the anode discharge potential on the passage of the alternating current becomes prominent. When Pt black is the cathode, the anode discharge potential diminishes, and the cathode discharge potential increases on the passage of the alternating current. Here too the increase in the cathode potential becomes much pronounced at voltages below the break which is noticed at about 2.55 volt.

TABLE XX.

The electrolytic cell consists of electrodes of Pt 2 sq. cm. each in a normal solution of NaOH.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0270 | 0.0345 | -1.940 | -1.620 | +1.030 | +0.980 |
| 2..... | 0.0125 | 0.0195 | -1.840 | -1.570 | +0.990 | +0.930 |
| 3..... | 0.0075 | 0.0135 | -1.790 | -1.570 | +0.970 | +0.910 |
| 4..... | 0.0030 | 0.0060 | -1.500 | -1.760 | +0.930 | +0.860 |
| 5..... | 0.0020 | 0.0020 | -1.200 | -1.300 | +0.900 | +0.800 |

At first the discharge potential at both the electrodes diminishes on the passage of the alternating current. But under conditions of very low current density the cathode discharge potential increases on the passage of an alternating current. The peculiar point was always noticed, that when the strength of the direct current passing through the circuit, was very small, the alternating current produced no change in the magnitude of the direct current. The diminution in the value of the discharge potential at one of the electrodes, was counterbalanced by its increase at the other electrode. This phenomenon occurs at only voltages below that corresponding to a break in the current potential curve. The effect of an alternating current on the electrolysis of solutions of a large number of electrolytes was studied in the elaborate manner indicated before, and the results obtained with some of the typical ones only have been given. Table XXI, however, which gives an account of the results obtained, when the source of the electrolytic current has a definite potential, *viz.*, 4 volt, show to what extent the various electrolytes agree in their behavior.

In the case of the oxidizing and the reducing salts the diminution in the anode potential on the passage of the alternating is always very prominent. In the case of the other salts such as sulfates and carbonates the effect of the alternating current is not so marked on the anodic discharge potential. Of course this relation holds good only when electrodes of platinum are used; if, however, a large foil of Pt black is used as one of the electrodes an alternating current does not much affect the discharge potential on its surface.

TABLE XXI.

| Cell. | Sq. cm. electrode. | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--|--------------------|---------------------------|--------|--------------------------|--------|------------------------|--------|
| | | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| Pt, NaNO_3 0.5 <i>N</i> , Pt..... | 8 | 0.0430 | 0.0450 | -1.440 | -1.420 | +0.620 | +0.590 |
| Pt, NaNO_3 0.2 <i>N</i> , Pt..... | 1.5 | 0.0320 | 0.0380 | -1.900 | -1.750 | +0.950 | +0.870 |
| Pt, KClO_3 0.2 <i>N</i> , Pt..... | 8 | 0.0215 | 0.0235 | -1.640 | -1.590 | +1.670 | +1.636 |
| Pt, KClO_3 0.2 <i>N</i> , Pt..... | 1.5 | 0.0130 | 0.0200 | -1.900 | -1.700 | +1.800 | +1.700 |
| Pt, KBrO_3 0.2 <i>N</i> , Pt..... | 8 | 0.0290 | 0.0340 | -1.100 | -0.940 | +1.900 | +1.830 |
| Pt, KBrO_3 0.2 <i>N</i> , Pt..... | 1.5 | 0.0150 | 0.0280 | -1.700 | -1.590 | +1.900 | +1.840 |
| Pt, $\text{Ba}(\text{NO}_3)_2$ 0.2 <i>N</i> , Pt.... | 8 | 0.0205 | 0.0250 | -1.600 | -1.470 | +1.700 | +1.650 |
| Pt, NaCOOH 0.2 <i>N</i> , Pt.... | 8 | 0.0250 | 0.0270 | -1.580 | -1.540 | +1.350 | +1.310 |
| Pt, NaCOOH 0.2 <i>N</i> , Pt.... | 1.5 | 0.0200 | 0.0250 | -1.660 | -1.530 | +1.470 | +1.370 |
| Pt, $\text{NaC}_2\text{H}_3\text{O}_2$ 0.2 <i>N</i> Pt.. | 8 | 0.0175 | 0.0210 | -1.650 | -1.590 | +1.62 | +1.540 |
| Pt, $\text{NaC}_2\text{H}_3\text{O}_2$ 0.2 <i>N</i> , Pt.. | 1.5 | 0.0130 | 0.0212 | -1.780 | -1.620 | +1.750 | +1.530 |
| Pt, Na_2SO_3 0.5 <i>N</i> , Pt..... | 8 | 0.0220 | 0.0238 | -1.360 | -1.360 | +1.730 | +1.660 |
| Pt, Na_2SO_3 0.5 <i>N</i> , Pt..... | 1.5 | 0.0160 | 0.0220 | -1.500 | -1.410 | +1.800 | +1.650 |
| Pt, Na_2HPO_4 0.5 <i>N</i> , Pt.... | 8 | 0.0230 | 0.0255 | -1.360 | -1.360 | +1.620 | +1.530 |
| Pt, Na_2HPO_4 0.5 <i>N</i> , Pt.... | 1.5 | 0.01450 | 0.0208 | -1.700 | -1.550 | +1.720 | +1.550 |
| Pt, $(\text{NH}_4)_2\text{SO}_4$ 0.5 <i>N</i> , Pt.... | 8 | 0.0250 | 0.0270 | -1.390 | -1.320 | +1.6 | +1.6 |
| Pt, $(\text{NH}_4)_2\text{SO}_4$ 0.5 <i>N</i> , Pt.. | 1.5 | 0.0165 | 0.0230 | -1.600 | -1.370 | +1.740 | +1.710 |
| Pt, MgSO_4 0.5 <i>N</i> , Pt..... | 8 | 0.0260 | 0.0273 | -1.300 | -1.270 | +1.630 | +1.620 |
| Pt, MgSO_4 0.5 <i>N</i> , Pt..... | 1.5 | 0.0122 | 0.0180 | -1.840 | -1.630 | +1.700 | +1.660 |
| Pt, Na_2CO_3 0.5 <i>N</i> , Pt..... | 8 | 0.0213 | 0.0236 | -1.830 | -1.750 | +1.460 | +1.470 |
| Pt, Na_2CO_3 0.5 <i>N</i> , Pt..... | 1.5 | 0.0125 | 0.0170 | -1.960 | -1.780 | +1.710 | +1.720 |

Influence of the Density of the Alternating Current.—It has been observed before, how the diminution in the discharge potentials depends on the density of the alternating current; for the purpose of determining this factor, the area of the electrodes was varied, and an alternating current of almost constant value was sent through the circuit. This method has the disadvantage that the discharge potential, due to the direct current, increases when the electrodes were made smaller. To eliminate this difficulty, the surface of the electrodes was kept constant in area, but the external metallic resistance was varied. Care was taken that the current strength through the primary of the induction coil remained constant throughout. The results obtained are given in Tables XXII, XXIII, and XXIV. It will be at once evident from these tables that the greater the resistance of the circuit, the less is the effect of the alternating current on the discharge potentials at the electrodes.

An Alternating Current Exerts Its Action on the Surface of the Electrodes Only.—It has been observed above to be a general phenomenon that when an alternating current is impressed along with a direct current to an electrolytic cell the discharge potential at the surface of the electrodes is a good deal diminished. The question however, arises whether the sinuoidal current thus produced by the conjugation of the direct with the alternate current has the property of keeping the discharge

TABLE XXII.

Electrodes of Pt (8 sq. cm.) 0.5 M H_2SO_4 sol. The source of the electrolytic current is a battery of 4 volts always.

| Total resistance. Ohms. | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|----------------------------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 50..... | 0.0370 | 0.0400 | -1.090 | -0.950 | +1.620 | +1.610 |
| 67..... | 0.0260 | 0.0280 | -1.050 | -0.930 | +1.600 | +1.590 |
| 107..... | 0.0160 | 0.0170 | -1.000 | -0.920 | +1.590 | +1.590 |
| 257..... | 0.0068 | 0.0073 | -0.970 | -0.910 | +1.560 | +1.560 |

TABLE XXIII.

Same as preceding, but electrodes 2.2 sq. cm.

| | | | | | | |
|----------|--------|--------|--------|--------|--------|--------|
| 50..... | 0.0325 | 0.0380 | -1.010 | -0.770 | +1.850 | +1.820 |
| 67..... | 0.0235 | 0.0280 | -1.000 | -1.770 | +1.780 | +1.770 |
| 107..... | 0.0150 | 0.0175 | -0.940 | -0.750 | +1.720 | +1.715 |
| 250..... | 0.0070 | 0.0075 | -0.850 | -0.720 | +1.630 | +1.625 |

TABLE XXIV.

Two electrodes of Pt (8 sq. cm.) in 0.1 N HCl .

| | | | | | | |
|----------|--------|--------|--------|--------|--------|--------|
| 47..... | 0.0315 | 0.0345 | -1.090 | -1.040 | +1.750 | +1.670 |
| 66..... | 0.0230 | 0.0245 | -1.080 | -1.030 | +1.700 | +1.660 |
| 106..... | 0.0142 | 0.0150 | -1.050 | -1.020 | +1.660 | +1.630 |
| 247..... | 0.0063 | 0.0063 | -1.030 | -1.020 | +1.580 | +1.570 |

potentials at a low value, analogous to that possessed by an intermittent current, or whether the alternating current exerts any specific action on the electrodes quite independent of the direct current. In order to settle this point it is necessary to isolate the alternating current from the direct current, to arrange the experiments in such a manner, that the alternating current should act on the surface of the electrodes only, but should on no account pass through the whole circuit. For the purpose the electrolytic cell was thus modified.

Each electrode was made of two metal foils dipped in the electrolyte very close to one another and connected through a key and a suitable resistance to the terminals of the secondary coil. The resistance of the main circuit was so adjusted that when the auxiliary electrodes were connected to the primary electrodes, no increase in the value of the direct current was observed. The resistance of the electrolyte between a primary and an auxiliary electrode was so small, that almost the entire alternating current passed through them. The advantage of this ar-

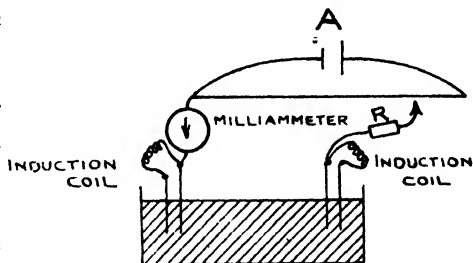


FIG. 4.

rangement lies in the fact, that the alternating current acts independently of the direct current, and that the effect of the alternating current on each of the electrodes could be studied separately.

TABLE XXV.

Two anodes of Pt (1 sq. cm.), two cathodes of Pt (3 sq. cm.), the electrolyte 0.5 N H_2SO_4 . Alternating current only passed through the anodes.

| | Strength of current. Amp. | | E. P. at cathode. Volt. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0270 | 0.0295 | -0.910 | -0.940 | +1.730 | +1.580 |
| 2..... | 0.0215 | 0.0232 | -0.840 | -0.870 | +1.680 | +1.580 |
| 3..... | 0.0170 | 0.0190 | -0.840 | -0.855 | +1.670 | +1.570 |
| 4..... | 0.0127 | 0.0147 | -0.830 | -0.850 | +1.660 | +1.550 |
| 5..... | 0.0064 | 0.0077 | -0.830 | -0.880 | +1.620 | +1.500 |
| 6..... | 0.0040 | 0.0052 | -0.800 | -0.840 | +1.600 | +1.490 |
| 7..... | 0.0014 | 0.0018 | -0.750 | -0.820 | +1.550 | +1.440 |

The effect of passing the alternate current through the anodes is to diminish markedly the discharge potential at that electrode. There is a simultaneous increase in the cathode discharge potential. This increase is to be attributed to the greater amount of current passing through the circuit. During conditions of very low current density the decrease in potential at the anode due to the alternating current is almost counter-balanced by a simultaneous increase at the kathode.

TABLE XXVI.

Two cathodes (1 sq. cm.) and two anodes (3 sq. cm.) in 0.5 N H_2SO_4 . The alternating current only plays between the cathodes.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0254 | 0.0325 | -1.050 | -0.650 | +1.660 | +1.660 |
| 2..... | 0.0178 | 0.0250 | -1.040 | -0.620 | +1.650 | +1.670 |
| 3..... | 0.0135 | 0.0225 | -1.020 | -0.500 | +1.630 | +1.660 |
| 4..... | 0.0100 | 0.0185 | -0.980 | -0.470 | +1.610 | +1.640 |
| 5..... | 0.0060 | 0.0135 | -0.890 | -0.450 | +1.590 | +1.630 |
| 6..... | 0.0036 | 0.0095 | -0.800 | -0.420 | +1.560 | +1.610 |
| 7..... | 0.0012 | 0.0060 | -0.750 | -0.390 | +1.520 | +1.600 |
| 8..... | 0.0010 | 0.0040 | -0.570 | -0.370 | +1.500 | +1.580 |
| 9..... | 0.0009 | 0.0013 | -0.340 | -0.280 | +1.470 | +1.510 |

The effect of the alternating current is far more marked at the cathode than at the anode. The cathode discharge potential diminishes very considerably while the anode discharge potential increases, during the play of the alternating current between the cathodes.

TABLE XXVII.

Two cathodes of Pt (1.25 sq. cm.) two anodes of Pt (1.5 sq. cm.) 0.5 *M* H₂SO₄. The alternating current passes through the cathodes as well as the anodes.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0205 | 0.0332 | -1.140 | -0.600 | +1.650 | +1.500 |
| 2..... | 0.0140 | 0.0240 | -1.020 | -0.580 | +1.630 | +1.500 |
| 3..... | 0.0108 | 0.0198 | -0.940 | -0.560 | +1.600 | +1.490 |
| 4..... | 0.0065 | 0.0158 | -0.930 | -0.520 | +1.590 | +1.490 |
| 5..... | 0.0038 | 0.0110 | -0.830 | -0.490 | +1.570 | +1.490 |
| 6..... | 0.0022 | 0.0072 | -0.820 | -0.470 | +1.550 | +1.490 |
| 7..... | 0.0010 | 0.0045 | -0.630 | -0.420 | +1.520 | +1.480 |
| 8..... | 0.0008 | 0.0020 | -0.450 | -0.390 | +1.460 | +1.450 |

Some peculiar points could be noticed in Table XXVII. The anode potential diminishes, on the passage of an alternating current only down to a definite value, *viz.*, 1.49 volt. The cathode discharge potential diminishes continuously and the diminution is much larger in amount.

TABLE XXVIII.

Two cathodes of Hg (0.75 sq. cm.), two anodes of Pt (2 sq. cm.) in 0.5 *M* H₂SO₄. The alternating current only passes through the cathodes.

| | Strength of current. Amp. | | E. P. at cathode. Volts. | | E. P. at anode. Volts. | |
|--------|------------------------------|--------|-----------------------------|--------|---------------------------|--------|
| | DC. | DC+AC. | DC. | DC+AC. | DC. | DC+AC. |
| 1..... | 0.0110 | 0.0210 | -1.560 | -1.020 | +1.770 | +1.820 |
| 2..... | 0.0045 | 0.0130 | -1.400 | -0.870 | +1.710 | +1.740 |
| 3..... | 0.0022 | 0.0082 | -1.230 | -0.700 | +1.610 | +1.680 |

The results obtained are quite analogous to those recorded in Table VII, where the alternating current passes along with the direct current in a cell having mercury as cathode and Pt as anode.

In Tables XXIX and XXX, in the experiments marked (a) only the direct current passes; in those marked (b), an alternating current plays between the cathodes; in those marked (c) the alternating current passes through the anodes only and in (d) through both.

The effect on the value of the direct current is greatest when the alternating current passes both through anodes and cathodes. The effect is least when the alternating current passes through the anodes only. In the former case, there is at first a diminution in the discharge potentials at both the electrodes but under conditions of very low current density produced by diminishing the voltage of the electrolytic current, the diminution in the anode discharge potential continues; but the cathode discharge potential remains constant or even increases. In the latter case, the discharge potential at the anode diminishes while that at the cathode increases from the very beginning. Similarly, by the passage of an alter-

nating current through the cathodes only, the discharge potential at that electrode only diminishes.

TABLE XXIX.

Two cathodes of Pt (2 sq. cm.) and two anodes of Pt (2 sq. cm.), in 0.5 *M* Na₂SO₄.

| | Strength of current. Amp. | | | | E. P. at cathode. Volts. | | | |
|--------|---------------------------|--------|--------|--------|--------------------------|--------|--------|------|
| | a. | b. | c. | d. | a. | b. | c. | d. |
| 1..... | 0.0195 | 0.0255 | 0.0240 | 0.0280 | -1.980 | -1.860 | -2.040 | .913 |
| 2..... | 0.0095 | 0.0140 | 0.0125 | 0.0160 | -1.910 | -1.810 | -1.950 | .850 |
| 3..... | 0.0055 | 0.0088 | 0.0081 | 0.0115 | -1.760 | -1.690 | -1.850 | .750 |
| 4..... | 0.0040 | 0.0060 | 0.0041 | 0.0065 | -1.590 | -1.520 | -1.650 | .580 |
| 5..... | 0.0030 | 0.0030 | 0.0030 | 0.0030 | -1.230 | -1.200 | -1.330 | .250 |

| E. P. at anode. Volts. | | | | |
|------------------------|--------|--------|--------|--------|
| | a. | b. | c. | d. |
| 1..... | +1.850 | +1.880 | +1.700 | +1.780 |
| 2..... | +1.670 | +1.700 | +1.570 | +1.620 |
| 3..... | +1.630 | +1.640 | +1.500 | +1.530 |
| 4..... | +1.550 | +1.570 | +1.480 | +1.510 |
| 5..... | +1.540 | +1.570 | +1.430 | +1.520 |

TABLE XXX.

Two cathodes of Pt (2 sq. cm.) two anodes of Pt (2 sq. cm.) in 0.1 *N* NaOH.

| | Strength of current. Amp. | | | | E. P. at cathodes. Volts. | | | |
|--------|---------------------------|--------|--------|--------|---------------------------|--------|--------|--------|
| | a. | b. | c. | d. | a. | b. | c. | d. |
| 1..... | 0.0240 | .. | 0.0275 | 0.0330 | -2.010 | .. | -2.080 | -1.830 |
| 2..... | 0.0128 | 0.0220 | 0.0175 | 0.0252 | -1.910 | -1.550 | -1.950 | -1.630 |
| 3..... | 0.0073 | 0.0155 | 0.0120 | 0.0178 | -1.810 | -1.460 | -1.900 | -1.600 |
| 4..... | 0.0038 | 0.0095 | 0.075 | 0.0122 | -1.590 | -1.310 | -1.760 | -1.410 |
| 5..... | 0.0028 | 0.0058 | 0.0045 | 0.0083 | -1.360 | -1.210 | -1.600 | -1.300 |

| E. P. at anode. Volts. | | | | |
|------------------------|--------|--------|--------|--------|
| | a. | b. | c. | d. |
| 1..... | +1.520 | .. | +1.350 | +1.430 |
| 2..... | +1.350 | +1.500 | +1.190 | +1.330 |
| 3..... | +1.230 | +1.390 | +1.010 | +1.170 |
| 4..... | +1.110 | +1.240 | +0.870 | +1.070 |
| 5..... | +1.080 | +1.140 | +0.810 | +0.990 |

The results obtained with caustic soda solution are quite similar to those obtained with the sodium sulfate solution. Solutions of several other electrolytes were examined in the same way. The following relations seem to hold good generally: When the alternating current passes through cathodes, the cathode discharge potential diminishes, while there is a simultaneous increase in the anode discharge potential; when the alternating current passes through anodes, the reverse phenomenon happens; when the alternating current passes through both, the discharge potential at both the electrodes at first diminishes, but at very low current densities such is not always the case.

Conclusions.

From the above results it is quite obvious, that the alternating current need not be impressed on an electrolytic cell in conjugation with a direct current, in order to produce its marked effect on the discharge potentials at the electrodes. The alternating current acts primarily on the surfaces of the electrodes. Of course it is very difficult to suggest how it facilitates the liberation of the ions at the electrode surface, since we have not got very definite views as to the cause of the overvoltage phenomenon. It is not easy to imagine how an alternating current can destroy the super-saturation on the electrode surface, which is generally ascribed to be the cause of the overvoltage. The hypothesis that the alternating current somehow alters the nature of the electrode surface appears to be most reasonable. Ruer¹ has observed that platinum passes into solution when it is acted upon simultaneously by a direct and an alternating current. Under the conditions, in which the experiments described in this paper were carried out, such was not found to be the case. The weight of a platinum foil which had been used in the course of many of the above experiments remained absolutely constant.

Newbury, in his very recent work,² holds that the ions first penetrate into the interior of the electrodes and there get discharged. The molecules thus produced from the ions, have not, like the ions, got free passage through the material of the electrodes. They accumulate inside the electrode, and only at very high pressures they come out by boring tunnels through the electrode surface. Now any process which facilitates this disruption of the electrode surface, will diminish the discharge potential on the electrodes. An alternating current of considerable intensity could easily be imagined to brush aside all the mechanical resistances offered to the passage of the molecules out of the electrode surface. The liberation of the ions are thus greatly facilitated and hence the discharge potential sinks.

Summary of this Paper and the Previous Communication.³

1. When an alternating current of high frequency, about 30000 per minute, passes through a cell consisting of two platinum electrodes dipped in any electrolyte, the electrode potentials change, thus indicating that some chemical action at the electrode surface takes place in that short amount of time.
2. When an alternating current passes through a reversible voltaic cell, there is no change in the electrode potential. If, however, one of the electrodes consists of a metal covered with its insoluble salts, the alternating current has pronounced effect on that electrode.

¹ *Z. physik. Chem.*, **44**, 81 (1903).

² *J. Chem. Soc.*, 1419 (1914).

³ *THIS JOURNAL*, **36**, 2333 (1914).

3. A greater amount of current could be supplied by a cell with one reversible and another irreversible electrode, when an alternating current plays in the circuit.

4. In cells like $\text{Cd-ZnCl}_2\text{-Hg}$, $\text{Cd-ZnCl}_2\text{-Pt}$, etc., the E. M. F. of Hg or Pt electrode approaches the value of the zinc electrode on the passage of the alternating current.

5. In perfectly reversible electrolytic cells the alternating current has no action when impressed on the cell along with a direct current.

6. But if the electrolytic cell be irreversible, the alternating current greatly increases the current strength through the circuit.

7. This increase in current strength is due to the diminution in the back electromotive force of polarization.

8. This diminution in the discharge potential is also observed, in electrolytic cells consisting of two cathodes and two anodes, the alternating current playing between the anodes or the cathodes, but not passing through the whole circuit.

In conclusion, my best thanks are due to Professors P. C. Rây, and J. B. Bhaduri, for their interest and encouragement.

CALCUTTA, INDIA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

PROPERTIES OF SILVER IODIDE INTERPRETED IN RELATION TO RECENT THERMODYNAMIC CONCEPTIONS.

BY GRINNELL JONES AND MINER LOUIS HARTMANN.

Received February 8, 1915.

This paper presents the results of an experimental study of the most important thermodynamic properties of silver iodide, interpreted in the light of Richards' Theory of Compressible Atoms. These results have also furnished a quantitative test of the so-called Nernst Heat Theorem. They support the former theory, but not the latter.

The mathematical physicists who developed the kinetic theory of gases and liquids, in order to simplify the exceedingly complex mathematical analysis, were forced to assume that atoms are incompressible. Theodore William Richards¹ has, however, presented an array of facts and arguments which show that atoms and molecules are, in reality compressible, or, in other words, that the volume of the atoms is changeable, and dependent on the pressure exerted upon them, whether due to (1) external force, (2) the attraction between molecules of the same kind, which is manifested in cohesion, (3) the attraction of the atoms within the

¹ Professor Richards, in a Presidential Address for the American Chemical Society, "The Present Aspect of the Hypothesis of Compressible Atoms" (THIS JOURNAL, 36, 2417 (Dec., 1914)), gives a summary of the results obtained and a complete bibliography.

molecules, which is manifested in chemical affinity. Richards has shown also that the free space within the molecules has been commonly greatly overestimated, and that it is in all probability very small.

The old kinetic hypothesis, with its added assumption that the volume of the atom is unchangeable, accounts for the fact that the coefficient of expansion of all substances (with five known exceptions) is positive by the assumption that, with rising temperatures, the increased violence of the molecular collisions causes an increase in the free space between the molecules. A decrease in volume with rise in temperature, *i. e.*, a negative coefficient of expansion, is, however, entirely inexplicable on this conception of the nature of the atom. But the coefficient of expansion of silver iodide is negative.¹

The senior author of this paper has attempted to account for this negative coefficient of expansion of silver iodide by an extension of this hypothesis of atomic compressibility. It was suggested² that the change in volume which occurs when a solid is heated may be regarded as made up of at least three parts:

1. An increase in the intramolecular free space. This effect is, however, probably small, since the free space itself is probably very small.
2. An increase in the volume of the molecules due to a decrease in the cohesion.
3. A change in the volume of the atoms due to a change in the attractive force between the molecules.

In the case of silver iodide, whose volume decreases with rise in temperature, this hypothesis led to the inference that the attractive force increases with rise in temperature, and thereby produces an increased compression great enough to outweigh the effect of the first two influences.

Although the free energy of the reaction may not give a quantitative measure of the attractive force, since a part of the work done by the attractive force or chemical affinity may be expended in producing compression of the atoms, and thereby be stored up as potential energy within the compound and not be available for outside work, nevertheless, the free energy gives the best indication we have of the attractive force, and would be expected to have the same temperature coefficient as the attractive force itself.

A computation of the temperature coefficient of the free energy by the aid of the Helmholtz equation indicated that free energy and, therefore, also, affinity does really increase with rise in temperature, and thus the deduction from the hypothesis was confirmed.

¹ See Grinnell Jones, *THIS JOURNAL*, 31, 191 (1909) for a discussion of the experimental evidence for this statement, and for a brief discussion of the four other known cases of negative coefficient of expansion.

² Grinnell Jones, *Loc. cit.*

The data used in these earlier computations were collected from many sources, and the errors of all of them entered into the result.¹ It, therefore, seemed desirable to further test this explanation of the negative coefficient of expansion of silver iodide by direct measurement at two temperatures of the potential of an electrolytic cell, which, by its action, produces silver iodide from its elements. A detailed description of this experimental study is given in the following pages.

In order to be able to apply accurately corrections for osmotic work, and for the liquid junction potential, a knowledge of the mobilities and concentrations of all the ions in the solution, at the two temperatures involved, is required. The existing literature furnished this desired information at 25°² but for 0° it was necessary to determine the mobility of I⁻ and I₃⁻ ions, and the concentrations of each ion in the solutions of different strengths of potassium iodide saturated with iodine. The special investigation carried out for this purpose has recently been published.³

The Free Energy of Formation of Silver Iodide.

In order to measure the free energy of formation of silver iodide from silver and iodine, a reversible electrolytic cell was devised, which by its action forms silver iodide from the elements. The electromotive force of this cell (after making certain corrections to the observed potential) gives a measure of the tendency of the reaction to occur. The cell consisted of two halves, an iodine electrode and a silver-silver iodide electrode. The iodine electrode consisted of a platinum foil surrounded by solid iodine in a solution of potassium iodide. Some of the dissolved iodine formed the triiodide ion from the iodide ion. The silver-silver iodide electrode was made of a platinum wire covered with silver and silver iodide in a solution of potassium iodide of the same strength as that used around the iodine electrode.

The action may be considered as, first, the solution of the silver to form silver ion, but since the solution is already saturated with silver iodide, this silver ion is immediately precipitated as AgI by the excess of iodide ion in the solution. Simultaneously, an iodide ion is formed from the iodine at the platinum electrode. The result is a difference of potential, which gives a measure of the tendency of silver and iodine to combine. Proper corrections must be applied for the potential at the junction of the two halves of the cell and for the osmotic work caused by the different concentrations of iodide ions on the two sides.

Details of the Experiments.—The potentiometer used was of the usual

¹ The heat of formation of silver iodide given by Thomsen was obtained very indirectly by him by the combination of a large number of thermo-chemical data, so that this result seemed especially unreliable.

² Bray and MacKay, *THIS JOURNAL*, 32, 914 (1910).

³ Jones and Hartmann, *Ibid.*, 37, 241 (1915).

Poggendorf compensation type, constructed of standardized Leeds and Northrup decade resistance boxes. The Weston standard cell was tested by the Bureau of Standards. The potentiometer gave entire satisfaction. It was sensitive to 0.01 millivolt on cells of low internal resistance, such as two similar platinum electrodes about 1 cm. apart in a 0.1 *N* solution of potassium iodide saturated with iodine. When using our complete silver-silver iodide-iodine cell, which had a very much greater internal resistance, readings could still be made with ease and certainty to 0.1 millivolt.

The cells were deeply immersed in a mixture of finely cracked ice and distilled water contained in a large Dewar tube, which was carefully covered with many inches of cloth. The rate of gain of heat from the surroundings was so slow that no stirring was necessary to maintain the temperature accurately at 0°. For the measurements at 25°, the cells were placed in a large electrically controlled thermostat, which was carefully adjusted to 25.00°, by the aid of a thermometer which had been calibrated at the Bureau of Standards. Since a change of 1° in temperature changes the potential of the cell by only 0.18 millivolt, it was easy to control the temperature so accurately that no error need be feared from this source.

Preparation of Chemicals and Solutions.—Iodine and potassium iodide were prepared as described on pages 242, 243, of our first paper.¹

Silver oxide was prepared from pure silver nitrate recrystallized twice from conductivity water and drained centrifugally. Barium hydroxide, found by test to be free from halogens, was dissolved in water and allowed to stand until the barium carbonate had settled. The solution was then poured through a filter into a dilute solution of the purified silver nitrate. At the end a very slight excess of the silver nitrate remained, and the precipitate was washed free from barium and nitrate. The precipitate was not dried, but was kept under water for future use.

Silver iodide was made by precipitating pure silver nitrate with pure potassium iodide in dilute solution and washing free from potassium nitrate solution. This salt was also kept moist in the form of a paste, protected from decomposition due to light.

The solutions of potassium iodide and of potassium iodide saturated with iodine were prepared as described in the first paper. The solutions were ordinarily saturated with iodine at 25°, and since solid iodine is precipitated readily from such solutions on cooling, the solution would adjust its own iodine content at 0° when cooled. By trial it was found that this method gave the same results as when the iodine solution was saturated at 0°. In all cases, the platinum electrode was covered with solid iodine so that the solution must have been in equilibrium at the temperature under consideration.

¹ Jones and Hartmann, *Loc. cit.*

Preparation of the Silver-Silver Iodide Electrodes.—The problem of preparing constant and reproducible silver electrodes was solved only after many trials and failures, which need not be described in detail. After many less satisfactory procedures had been tried, the following was found to give very good electrodes: A platinum wire was sealed into a small glass tube so that outside connection could be made through mercury in the tube. The end of the platinum wire was wound into a small spiral and carefully cleaned. Silver was then electroplated onto the platinum from a solution of silver nitrate in potassium cyanide. A very small current—about 0.005 amperes for each electrode—was used for two hours. The electrode was then carefully washed free from cyanide, and dipped into a thick paste of silver oxide and water. The silver oxide on the wire was decomposed by slowly heating in a small electric oven at from 400° to 500°. It was found to be necessary to entirely decompose the silver oxide, or a different electromotive force was obtained. The silver oxide was applied several times and heated, until the spiral was filled with this finely divided but still coherent mass of silver.¹ The electrode was next made an anode in a dilute solution of potassium iodide, and thus coated with a very thin, coherent layer of silver iodide.² The current used in this operation was only 0.001 ampere, and the time was about two hours. The electrodes were allowed to stand in a fresh solution of potassium iodide, saturated with silver iodide, of the same strength as that in which they were to be used.

To show the reproducibility of this form of electrode, the following table will be sufficient. Electrodes 42, 44, 45 were made June 20th; 50 and 51 were made together June 27th; 63 and 64 were made July 1st. Nos. 42 and 51 had been in contact with potassium iodide containing free iodine. All had been used in various preliminary cells. These data were taken July 8th.

| | | | | | | |
|-------------------|----------|----------|----------|----------|----------|---------------|
| No. 64 against... | 45 | 44 | 42 | 50 | 51 | 63 |
| Difference..... | +0.00024 | —0.00002 | +0.00024 | +0.00020 | +0.00003 | +0.00013 volt |

Average difference from the mean 0.00009 volts.

Considering the diverse treatment of these electrodes before this measurement, the agreement is quite satisfactory.

The following table will show the variation of five of these electrodes, prepared at the same time and under identical conditions. The measurements were made with the electrodes dipping into a 0.1 *N* solution of potassium iodide saturated with silver iodide.

| | | | | |
|--|----------|----------|---------|---------------|
| No. 61 against..... | 62 | 63 | 64 | 65 |
| Difference..... | —0.00002 | —0.00001 | 0.00000 | +0.00002 volt |
| Maximum difference between any pair..... | 0.00004 | | | |
| Average difference from mean..... | 0.00001 | | | |

¹ This procedure was used by Lewis, *THIS JOURNAL*, 28, 166 (1906), for silver electrodes in silver nitrate solution.

² H. M. Goodwin, *Z. physik. Chem.*, 13, 630 (1894), used this procedure with good results.

The Iodine Electrodes.—The iodine electrodes were made after the manner described by Crotogino.¹ A piece of platinum foil about 1 cm. square was welded to a short platinum wire. This wire was sealed through the end of a glass tube, so that electrical connection could be made through a column of mercury. The platinum wire and foil were thoroughly cleaned with acids and heated white hot before use. They were then put into a potassium iodide solution saturated with iodine.

Five electrodes made in this way at different times and used in preliminary cells gave the following results, after standing in a 0.1 *N* solution of potassium iodide saturated with iodine:

| | | | | |
|--|----------|----------|----------|---------------|
| No. 5 against..... | 24 | 6 | 11 | 21 |
| Difference..... | —0.00005 | —0.00006 | —0.00008 | —0.00004 volt |
| Maximum difference between any pair..... | 0.00008 | | | |
| Average difference from the mean..... | 0.00002 | | | |

Another set prepared and measured at a later time showed even better agreement. These electrodes were ignited in a gas flame to a white heat, and then allowed to stand short-circuited in a 0.1 *N* solution of potassium iodide saturated with iodine. The electrodes being close together, the internal resistance of the cell was low, and under these conditions our potentiometer was very sensitive, a change in the setting corresponding to 0.1 millivolt causing a deflection of 13 mm. on the scale of the galvanometer. It is evident that the iodine electrodes, if properly prepared and handled, need give us no anxiety.

No. 21 against:

| | | | | | | |
|-------------------------------------|---------|---------|----------|----------|----------|---------------|
| 22 | 23 | 24 | 25 | 26 | 27 | 28 |
| Difference: | | | | | | |
| 0.00000 | 0.00000 | 0.00000 | +0.00001 | —0.00005 | —0.00005 | —0.00005 volt |
| Maximum difference of any pair..... | | | | | | 0.00005 |
| Average difference from mean..... | | | | | | 0.00003 |

The Silver Iodide Cell.—The problem of preparing the electrodes having been solved, it now remained to find the best way to connect the two halves of the cell. The diffusion of iodine (or the triiodide ion) to the silver electrode must not occur for several days, the internal resistance of the cell must not become so great that our potentiometer would not be sensitive to 0.1 millivolt, and the conditions at the junction of the two liquids must approach, as nearly as possible, to the conditions which are assumed in the derivation of the equation, by which the potential at the liquid junction is calculated. The cells should be constant for a long time and reproducible. Cells were tried with the familiar double siphon connection, and also cells in which the connection was made in a U-tube filled with sand, but these cells were not as constant and reproducible as a cell of a much simpler construction in which the connection is made through

¹ Crotogino, *Z. anorg. Chem.*, **24**, 255 (1900).

a ground-glass stopper.¹ If the glass-grinding is very good, and the stopper firmly in place, the internal resistance is too great, and, therefore, the potentiometer not sufficiently sensitive, but by regrinding a very little with coarse carborundum, it was found to be possible to greatly increase sensitiveness of the potentiometer without causing unduly rapid diffusion of iodine to the silver electrode. Cells of this type were found to be appreciably more constant and reproducible than cells of any other type which were tried, and were used in all the final measurements. Planck, in the derivation of his formula for the potential at the boundary of two solutions, assumes that junction is sharp at the beginning, and that an intermediate layer of variable composition is produced by diffusion alone with *no mechanical mixing* of the solutions. This construction of the cell seems to realize this condition experimentally better than any other.

A sketch showing the construction of the type of cell which gave the most constant and reproducible results is shown in Fig. 1. The large outer tube was fitted with a rubber stopper through which the inner tube was inserted. Two holes were made in the stopper, large enough to allow the silver electrodes to be put through them, and a third small hole to allow equalization of air pressure was made. The silver electrodes were held in place by means of smaller rubber stoppers, which fitted into the holes in the main stopper. This arrangement allowed easy interchange of the electrodes without disturbing the cells. The inner tube had a ground-glass stopper at the end inside the cell. The upper end was provided with a paraffined cork stopper (which is not appreciably attacked by iodine vapors), which supported the iodine electrodes. The ground-glass stopper was held in place by a silver wire.

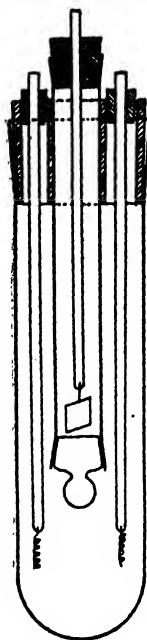


Fig. 1.

The large tube contained the potassium iodide solution saturated with silver iodide, and the inner tube contained the same solution saturated with iodine, and a large excess of solid iodine. In setting up the cell, the potassium iodide solution was first put in the outer tube and the saturated iodine solution, together with a large excess of solid iodine, put in the inner tube. The latter, with the large rubber stopper, was put into place as soon as the solution had wet the ground-glass joint, and the levels of the two solutions were quickly adjusted to avoid any difference of pressure. Then the iodine and silver electrodes were put in place and the whole apparatus made water proof with paraffin. It was then placed in the thermostat, and the potential measured.

¹ A. P. Laurie, *Z. physik. Chem.*, **64**, 617 (1908), has used a liquid junction of this kind with success.

The potential of the cells when first set up was variable and not reproducible, but after allowing a few hours for the temperature and the condition at the boundary to adjust themselves, this uncertainty disappeared. Several of the cells containing 0.1 *N* potassium iodide solution were kept at constant temperature for a week, and the potential did not vary more than 0.0002 volt, and they were apparently in good condition when the measurements were stopped. The cells containing 0.05 *N* solution were not quite so constant. Their variation was, however, not over 0.0004 volt during several days. With a pair of each kind of electrodes in a cell, it was possible to obtain check readings on the electrodes, and these seldom varied more than 0.0002 volt. In the case of the iodine electrodes it was hardly ever possible to detect any difference at all, and in the later experiments only one of these electrodes was used.

Two strengths of potassium iodide were used, 0.1 *N* and 0.05 *N*. Measurements of the potential at 0° and 25° were made with both strengths of solution. Tables I, II, III, IV will show measurements of typical cells under the four conditions.

Many other cells of the same type were set up, but since they behaved in a very similar way, it does not seem necessary to record the observations in detail. The accepted potential judged from each of these cells alone is given below, which records all the cells which were not subject to known error and which remained constant for a reasonable length of time. A considerable number of cells were set up which for one reason or another

TABLE I.—POTENTIAL OF CELL No. 4.
0.1 *N* KI SOLUTION, 25.0°. IODINE
ELECTRODE No. 1.

| Date. 1912. | Time. | Silver electrode No. 37. Volt. | Silver electrode No. 38. Volt. |
|-----------------------------------|------------|---|---|
| May 21 | 11:30 A.M. | 0.7017 | 0.7016 |
| May 21 | 4:30 P.M. | 0.7005 | 0.7003 |
| May 22 | 8:00 A.M. | 0.6999 | 0.7001 |
| May 22 | 8:45 P.M. | 0.7000 | 0.7002 |
| May 23 | 10:30 A.M. | 0.7000 | 0.7000 |
| May 24 | 1:00 P.M. | 0.6998 | 0.7000 |
| May 26 | 11:00 A.M. | 0.7001 | 0.7000 |
| Accepted potential from this cell | | 0.7000 | |

NOTE.—The first measurements (11:30 A.M., May 21) were made immediately after setting up the cell, and, therefore, are not significant. Even five hours later this cell had not reached its final potential.

TABLE II.—POTENTIAL OF CELL No. 31.
0.05 *N* KI SOLUTION, 25.0°. IODINE
ELECTRODE No. 5.

| Date. 1912. | Time. | Silver electrode No. 80. Volt. | Silver electrode No. 72. Volt. |
|---|-----------|---|---|
| July 19 | 4:00 P.M. | 0.6995 | 0.6996 |
| July 20 | 7:45 A.M. | 0.6989 | 0.6991 |
| July 20 | 7:30 P.M. | 0.6992 | 0.6994 |
| July 21 | 9:00 P.M. | 0.6992 | 0.6990 |
| July 22 | 1:00 P.M. | 0.6990 | 0.6991 |
| July 23 | 9:00 A.M. | 0.6991 | 0.6992 |
| July 24 | 6:00 P.M. | 0.6990 | 0.6992 |
| July 25 | 8:00 A.M. | 0.6984 | 0.6987 |
| Accepted potential from this cell..... | | 0.6992 | |

NOTE.—The measurements of July 19th were made immediately after setting up the cell, and are, therefore, not significant. By July 25th, the sixth day, some iodine had diffused over to the silver electrodes, and these measurements are, therefore, insignificant.

TABLE III.—POTENTIAL OF CELL No. 5.
0.1 *N* KI SOLUTION, 25.0° AND 0.0°.
IODINE ELECTRODE No. 3.

| Date | Time. | Silver electrode No. 39. Volt. | Silver electrode No. 40. Volt. |
|--|------------|---|---|
| Measurements at 25.0°: | | | |
| May 21 | 11:30 A.M. | 0.7016 | .. |
| May 21 | 8:00 P.M. | 0.7001 | 0.7000 |
| May 22 | 9:00 P.M. | 0.7001 | 0.6999 |
| May 23 | 10:30 A.M. | 0.6998 | 0.6997 |
| Cell put in ice after 10:30 measurement and the following measurements made at 0.0°: | | | |
| May 23 | 1:00 P.M. | 0.6948 | 0.6948 |
| May 23 | 8:00 P.M. | 0.6939 | 0.6938 |
| May 24 | 1:00 P.M. | 0.6936 | 0.6935 |
| May 25 | 10:30 P.M. | 0.6936 | 0.6935 |
| May 26 | 8:00 A.M. | 0.6934 | 0.6934 |

Accepted potential from this cell at

25° = 0.7000; at 0° = 0.6936

TABLE IV.—POTENTIAL OF CELL No. 35
0.05 *N* KI SOLUTION, 0.0°. IODINE
ELECTRODE No. 5.

| Date. | Time. | Silver electrode No. 80. Volt. | Silver electrode No. 72. Volt. |
|--|-----------|---|---|
| July 29 | 4:30 P.M. | 0.6922 | 0.6925 |
| July 30 | 8:30 A.M. | 0.6918 | 0.6920 |
| July 30 | 5:30 P.M. | 0.6920 | 0.6920 |
| July 31 | 12:00 M. | 0.6916 | 0.6919 |
| Aug. 1 | 2:00 P.M. | 0.6919 | 0.6922 |
| Aug. 2 | 3:30 P.M. | 0.6918 | 0.6921 |
| Aug. 3 | 8:00 A.M. | 0.6921 | 0.6918 |
| Aug. 4 | 9:00 A.M. | 0.6921 | 0.6918 |
| Accepted potential from this cell..... 0.6919 | | | |

NOTE.—Set up at room temperature
at 10:00 A.M. and put into ice bath.

did not give constant and reproducible results. In some of these, the ground joint connecting the two halves of the cell was so imperfect that free iodine diffused through to the silver electrode too quickly. In still others, the ground joint was so perfect that the internal resistance of the cell was so great that accurate measurements were not possible. Cells of entirely different construction, with the familiar siphon connections, and cells in which the connection was made in a U-tube filled with sand were also tried, but were found to be less satisfactory and were abandoned. The accepted potentials of the cells which were constant and not influenced by known errors are given below.

| 0.1 <i>N</i> KI soln. at 0° | | 0.05 <i>N</i> KI soln. at 0° | | 0.1 <i>N</i> KI soln. at 25° | | 0.05 <i>N</i> KI soln. at 25° | |
|--------------------------------|--------|---------------------------------|--------|---------------------------------|--------|----------------------------------|--------|
| Cell No. | Volt. | Cell No. | Volt. | Cell No. | Volt. | Cell No. | Volt. |
| 5 | 0.6936 | 29 | 0.6921 | 3 | 0.7000 | 27 | 0.6993 |
| 10 | 0.6935 | 32 | 0.6920 | 4 | 0.7000 | 30 | 0.6992 |
| 23 | 0.6936 | 33 | 0.6920 | 5 | 0.7000 | 31 | 0.6992 |
| Accepted | | 34 | 0.6919 | 21 | 0.7001 | Accepted | |
| av. | 0.6936 | 35 | 0.6919 | 23 | 0.7001 | av. | 0.6992 |
| | | Accepted | | Accepted | | | |
| | | av. | 0.6920 | av. | 0.7000 | | |

The Liquid Junction Potential.—Planck,¹ by reasoning based on kinetic considerations, has deduced a general differential equation for the liquid junction potential between two solutions which differ in concentration by infinitesimal amounts. In order to integrate this equation between limits

¹ M. Planck, *Wied. Ann.*, 39, 161 (1890); 40, 561 (1890).

representing the composition of the two solutions around the electrodes, Planck has made the following assumptions:¹

1. The intermediate layer is produced by diffusion alone.
2. The mobility of any given ion is the same in both end solutions, and through the intermediate layer.
3. The simple van't Hoff Law $\pi = cRT$ holds.

Planck's general equation is complex, and somewhat troublesome to use, but for the special case when the total ion concentration is the same on both sides of the junction and all the ions are univalent, this reduces to the equation,²

$$E = \frac{RT}{F} \ln \frac{U_2 + V_1}{U_1 + V_2}$$

where U_1 is the sum of the products of concentration and mobility of all the cations present in solution 1. U_2 is the same sum for the other solution. V_1 and V_2 are the corresponding quantities for the anions.

It now remains to consider how closely our actual cells approach each of the assumptions involved in the derivation of the formula.

Planck's reasoning is based on the assumption that the intermediate layer is produced by diffusion alone, *i. e.*, the two solutions are first brought together with a sharp boundary, and then an intermediate layer is produced by diffusion without mechanical mixing. He concludes that the rate of diffusion at first will be very great, but after diffusion has proceeded for a short time, the rate of diffusion becomes so small that the amount of diffusion is negligible in the time required to measure the potential. He also concludes that the potential is independent of the thickness of the intermediate layer, but depends only on the composition of the end solutions. A junction within a ground-glass joint, such as we used, seems to us to meet this condition as perfectly as it is possible to do so experimentally. Some of our cells, after showing a variable potential for the first hour or two after they were set up, remained constant for a week, which is quite in accord with Planck's conclusions from his mathematical analysis of the problem.

Henderson³ has attacked the problem by a thermodynamic process of

¹ Planck restricts his treatment to solutions in which all the ions are univalent. The more general case, which is much more complex mathematically, has been treated by Plejél, *Z. physik. Chem.*, **72**, 1 (1910), and by K. R. Johnson, *Ann. Physik.*, **14**, 995 (1904), but does not concern us for the present purpose.

² In our cells the concentration of the ions is not identical on the two sides of the junction, owing to a slight change in volume, which occurs on dissolving iodine, and to a slightly different degree of dissociation of potassium iodide and triiodide. We have, therefore, carried out the calculations with Planck's general equation, and obtained a result which differs by only 0.01 millivolt from the result given by the simplified form.

³ P. Henderson. *Z. physik. Chem.*, **50**, 118 (1907); **63**, 325 (1908).

reasoning. He derives the same differential equation for the potential between two solutions differing in concentration by infinitesimal amounts that Planck obtained by kinetic reasoning. In order to integrate this equation, he assumes that the intermediate layer is formed, not by diffusion, but by the mechanical mixing of the end solutions. The last two assumptions made by Planck must also be made in Henderson's deduction. For the general case, the liquid potentials calculated by Henderson's equation and Planck's equation are appreciably different, but for the special case, met with in our cells, namely, the two end solutions containing a common cation (K^+) at the same concentration, and differing only in the anions (I^- in one case, and a mixture of I^- and I_3^- in the other), Henderson's equation reduces to a form which is identical with Planck's equation. This shows that if a little mixing occurred in making our junction, it would not affect the results.

It seems probable that as the I_3^- ion and I_2 and KI molecules diffuse into the pure potassium iodide solution, the reversible reaction $I^- + I_2 \rightleftharpoons I_3^-$ may cause some change in the concentrations of the ions, and thus in effect change the nature of the intermediate layer. Since we do not know the relative rate of diffusion of the triiodide ion (I_3^-) and molecular iodine (I_2), it is not possible to determine the influence of this on the intermediate layer. It is, therefore, reassuring that the Planck and Henderson equations, which assume quite different intermediate layers, give identical results for our special case.

The second assumption is not strictly met by our cells, since there is a slight difference in the viscosity of the two solutions, but we have convinced ourselves by suitable computations that this effect is so small that it may safely be neglected.

The third assumption is not met exactly even by dilute solutions. The "activity," to use the term proposed by G. N. Lewis, is not strictly proportional to the concentration. In the light of our present knowledge, however, it does not seem feasible to avoid the error inherent in this assumption.¹

The values for the mobilities and concentrations of the ions used in this computation at 0° have been determined by a special investigation, carried out for the purpose, and recently published.² The corresponding data for 25° are based upon the data of Bray and MacKay,³ corrected for the effect of viscosity.²

¹ Experiments are under way, which, it is hoped, will throw more light on this question. But since this is a large problem in itself, which must require some time for completion, and since the outcome cannot affect the main conclusions of this paper, it has not seemed wise to postpone publication of the results already obtained, pending the outcome of this further study.

² Jones and Hartmann, *THIS JOURNAL*, *loc. cit.*

³ Bray and MacKay, *THIS JOURNAL*, **32**, 914 (1910).

The Osmotic Work Correction.—The measured potential of the silver iodide cell must be further corrected on account of the osmotic work. In the reaction in the cell, iodide ion is produced (at the iodine electrode) in a solution of one concentration with respect to this ion, while a corresponding amount of iodide ion is removed (as silver iodide) at the other electrode from a solution almost twice as concentrated in iodide ion. This involves some osmotic work, which is included in the measured potential of the cell, and must be taken into consideration.

The familiar Nernst concentration cell equation is the most accurate method, according to our present knowledge, of calculating this potential.

$$(E_2 - E_1) = RT/F \ln C'_I / C''_I.$$

C'_I = Concentration of iodide ion in potassium iodide solution.

C''_I = Concentration of iodide ion in same solution saturated with iodine.

This equation is obtained by the integration of a differential equation, which is derived thermodynamically and is doubtless accurate, but in order to integrate the equation in the form given, it is necessary to assume that the simple van't Hoff law holds. This assumption probably is not fulfilled exactly by our solutions, so that this correction may not be quite accurate. This potential due to osmotic work is in the same direction as the measured potential, and hence should be subtracted from the measured potential of the cell.

The potentials of the cell under the four conditions are given in Table V. In this table are also given the corrections which must be applied to the measured potentials, and the final corrected potentials, which represent the tendency of iodine and silver to combine with each other.

TABLE V.

| | At 0°. | | At 25°. | |
|---------------------------------------|---------|---------|----------|---------|
| | 0.1 N. | 0.5 N. | 0.1 N. | 0.5 N. |
| Measured potential (volts)..... | +0.6936 | +0.6920 | +0.7000 | +0.6992 |
| Liquid junction correction (volts)... | +0.0030 | +0.0029 | +0.00325 | +0.0032 |
| Osmotic work correction (volts)..... | -0.0154 | -0.0151 | -0.0180 | -0.0177 |
| Final corrected potential..... | +0.6812 | +0.6798 | +0.6852 | +0.6847 |
| Free energy (A) kilojoules..... | 65.73 | 65.60 | 66.12 | 66.07 |
| Free energy (A) kilogram calories... | 15.72 | 15.69 | 15.81 | 15.80 |

Temperature coefficient of electromotive force from measurements with 0.1 N solution = $(0.6852 - 0.6812)/25 = +0.000160$ volt per degree, equivalent to 15.5 mayers or 3.7 calories per degree.

Temperature coefficient of electromotive force from measurements with 0.05 N solution = $(0.6847 - 0.6798)/25 = +0.000196$ volt per degree, equivalent to 18.9 mayers or 4.5 calories per degree.

The difference between the results with 0.1 N and 0.05 N solutions is probably due to the fact that the activity of the ions is not proportional to the concentration, especially in the stronger solution. This subject

has been discussed in considerable detail by Bray and MacKay, whose conclusion is, "It is evident that, no matter what assumption is made, one or more of the substances involved will show marked deviations from the law of the ideal solution that activity and concentration are equal." Since these deviations are undoubtedly less in the more dilute solution, we regard the result obtained with the 0.05 *N* solution as the more reliable, although the result with the stronger solution furnishes a valuable confirmation.

These results show conclusively that the temperature coefficient of the free energy of formation of silver iodide is positive, and thus support the analysis of the coefficients of expansion based on Richards' hypothesis of compressible atoms, and furnish us with a reasonable explanation of this almost unique property of silver iodide.

Free Energy, Total Energy, and Heat Capacity.

His conception of the compressible atom led Richards¹ to some new fundamental ideas regarding the relationship between the attracting energy or chemical energy, the free energy or power of producing outside work, and the heat evolved during a reaction, when it proceeds isothermally and under such conditions that no outside work is done.

"When the heat capacity of a system does not change during a reaction, and concentration influences are balanced, the free-energy and total-energy changes of the reaction are equal and unchangeable with the temperature, and each may be supposed to represent the total 'attracting energy'—a term which covers gravitational and electrical attraction as well as purely chemical attraction."

Richards pointed out that the compression which usually occurs during a chemical reaction must diminish the heat capacity by restricting the vibrations, so that the heat present in the factors before the reaction is more than sufficient to raise the temperature of the products from absolute zero to the temperature of the reaction. Therefore, the heat evolved during the reaction, as measured in the usual way in a calorimeter, is greater than the heat produced from the chemical energy of the reaction. Or, in other words, the "Wärmetönung" is greater than the chemical energy. In such a case, the free energy is less than the chemical energy, since a part of the chemical energy is expended in producing the compression of the atoms, and is not available for outside work. Since $dU/dT = C_F - C_P$ (molecular heat capacity of factors minus molecular heat capacity of products), and C_F is greater than C_P , dU/dT will be positive. Richards reasoned that in such a case dA/dT is negative, and was able to support this conclusion by experimental evidence. The possibility of the converse case is also clearly indicated by Richards, although such cases are much rarer.

One of these converse cases is silver iodide, a most interesting substance

¹ *Proc. Amer. Acad.*, 38, 293 (1902).

from the standpoint of this hypothesis, because it has several exceptional properties, and one which is almost unique.¹ During the formation of silver iodide from its elements, there is an increase in volume of nearly 15% of the whole, in contrast to most salts, which show a decrease in volume during formation.² The molecular heat capacity of silver iodide is greater than the sum of the heat capacities of silver and iodine,³ which is also unusual, but is related to the increase in volume, as already pointed out in the discussion of the more common converse case. By reference to Table V, it will be seen that the free energy of formation of silver iodide (A) is 66.1 kilojoules at 25°. It is easily possible to compute by the Helmholtz equation from the data presented in Table V that the heat evolved (U) is 61.0 kilojoules. A is, therefore, greater than U. dU/dT is negative and dA/dT is positive, and the coefficient of expansion is negative. These facts in regard to silver iodide thus confirm conclusions which Richards drew from the hypothesis of compressible atoms in a complete and remarkable way. The case is all the more noteworthy, because the relations are just the converse of those usually met with, but it is nevertheless entirely consistent.

In order that a quantitative formulation of these relationships may be subjected to a rigid test in many cases, it is necessary to know the atomic and molecular heat capacities of both factors and products of the reactions under consideration from absolute zero up to the working temperatures. Richards and Jackson⁴ began the collection of the data on specific heats of solids down to liquid air temperatures, and in 1910 published results on twenty-six elements. These results showed that the specific heats are very much less at low temperatures than at room temperature.

Richards first published these new fundamental ideas in regard to the "Significance of Changing Atomic Volume" in 1902. Nernst⁵ attempted, in 1906, to give these ideas a mathematical formulation. But in doing this he made two assumptions which require experimental proof. These assumptions will be discussed in detail after Nernst's mathematical formulation has been followed to the point where these assumptions are necessary for further progress.

In his early papers, Nernst expressed the atomic or molecular heat capacities of solids as a function of temperature in the form of a rapidly

¹ Richards and Jones, *THIS JOURNAL*, 31, 186 (1909).

² Density..... Ag, 10.49 I, 4.993 AgI, 5.674
Molecular volume..... Ag, 10.28 I, 25.73 AgI, 41.38

41.38 — (10.28 + 25.73) = 5.37 cc. increase in volume during formation of salt.

³ A discussion of the experimental evidence for this statement will be found on a later page.

⁴ Richards and Jackson, *Z. physik. Chem.*, 70, 414 (1910).

⁵ Nernst, *Göttinger Nachrichten*, 1906, 1.

convergent polynomial series in powers of T , but this expression was later abandoned in favor of Einstein's specific heat formula, and this in turn was superseded by a new specific heat formula proposed by Nernst and Lindemann.

In 1907, Einstein¹ had derived the following expression for the atomic or molecular heat capacity of solids at constant volume as a function of the absolute temperature and the "vibration frequency" of the atoms (or electrons within the atoms).

$$C_v = 3R \sum \frac{(\beta \nu / T)^2 e^{\beta \nu / T}}{(e^{\beta \nu / T} - 1)^2}$$

C_v = atomic (or molecular) heat capacity at constant volume.

R = gas constant.

e = base of natural logarithms.

T = absolute temperature.

$\beta = 4.86 \times 10^{-11}$, a universal constant, whose numerical value was deduced by Planck from a study of radiation phenomena.

ν = vibration frequency theoretically, but in practice is usually selected empirically to make the formula fit the data as well as possible.

Σ = the summation sign which indicates that summation is to be extended over the vibrations of all the frequencies which are actually occurring.

This formula was deduced by applying the Quanten Hypothesis, which Planck formulated for the ether vibrations, to the vibrations of solids. The assumption is made that the atoms of a solid cannot take up heat continuously,² but only in units or "quanta," and that the magnitude of the units is proportional to the vibration frequency.

The heat capacity at constant volume (C_v) cannot, however, be determined experimentally. The heat capacity at constant pressure C_p , which can be experimentally determined, and is desired in the development of the theory, can, however, be computed from C_v by the following well known thermodynamic formula.

$$C_p = C_v + 9 \alpha^2 VT/K.$$

α = cubic coefficient of expansion (thermal).

K = coefficient of compressibility.

V = molecular volume.

Unfortunately we have little exact knowledge of α and K as functions of the temperature. Nernst and his co-workers replace the last term by $aT^{1/4}$ (where a is constant for any substance), pointing out that this accords with what we know in regard to the influence of temperature on α and K , and that this last term is small in comparison to the first term.

¹ Einstein, *Ann. Phys.*, [4] 23, 180 (1907).

² The word "continuously" is used in its mathematical sense.

This formula was found to be in agreement with the early results obtained in Nernst's laboratory by Nernst, Eucken, Pollitzer, Koref, and Lindemann, which extended to liquid air temperatures only.

When, however, the measurements were extended down to the temperature of liquid hydrogen, it was found that the experimental results were unmistakably higher than the results computed from the Einstein formula. Nernst and Lindemann¹ then proposed a modified formula

$$C_v = \frac{3}{2}R \sum \left\{ \frac{(\beta\nu/T)^2 e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2} + \frac{(\beta\nu/2T)^2 e^{\beta\nu/2T}}{(e^{\beta\nu/2T} - 1)^2} \right\} + \alpha T^{1/2},$$

which was found to fit the data very much better down to liquid hydrogen temperatures. This formula was originally found empirically, but Nernst and Lindemann point out that, if the assumption is made that the potential energy of the atom due to its separation from its position of rest is taken up in quanta which are one-half as great as the quanta of the kinetic energy, then this formula may be derived by reasoning very similar to that of Einstein. In the case of the metals it was only necessary to assume a single value for ν , and in the case of simple salts containing two elements, it was only necessary to assume two values of ν corresponding to the two kinds of atoms. Two values of ν are assumed in the case of sulfur and graphite, but only one for diamond. Three values of ν are assumed in the case of silica and mercurous sulfate.

According to this formula, the heat capacities approach zero as their limit, as the temperature approaches absolute zero. This remarkable result has been experimentally confirmed by Nernst² and Lindemann in the case of the diamond. According to this formula, C_v approaches $3R$ as its limit, as the temperature is raised. This is in entire accord with the conclusions reached previously by G. N. Lewis,³ that the deviations from Dulong and Petit's Law are due partly to the second term involving the heat absorbed during thermal expansion, and in the case of a few elements to the necessity of reaching high temperatures, before Dulong and Petit's Law holds. Moreover, we have convinced ourselves by suitable calculations, that the formula can be made to fit, at least approximately, the data of Richards and Jackson, and Griffiths and Griffiths.⁴

In the case of three salts (KCl, KBr and NaCl) the value of the vibration frequency may be computed from the measurements of the wave lengths of the residual rays (Reststrahlen) by Rubens and Hollnagel.⁵

¹ Nernst and Lindemann, *Sitzb. Akad. Wiss. Berl.*, 1911, 494; *Z. Elektrochem.*, 17, 817 (1911).

² Nernst and Lindemann, *Loc. cit.*

³ *THIS JOURNAL*, 29, 1165 (1907).

⁴ *Phil. Trans.*, (A) 213, 119 (1913); *Proc. Roy. Soc. London*, (A) 90, 557 (1914).

⁵ *Sitzb. Akad. Wiss. Berl.*, 1910, 26; *Vdlg. d. D. phys. Ges.*, 12, 83 (1910).

Since the other quantities in the formula are all known for these salts, it has been possible to compute the heat capacity without selecting any quantity empirically to fit the data. The calculated results accord with the observed within 1%, which must certainly be regarded as a great triumph for the formula.

The assumption of a single vibration frequency seems *a priori* very improbable in view of the fact that solids show a continuous spectrum. Three attempts to derive a specific heat formula with the aid of the Quanta theory, without using the simplifying assumption that one or two vibration frequencies only are involved, have been published by Debye,¹ Born and von Karman,² and von Juptner.³ Von Juptner's formula leads to negative values for C_v in certain intervals of temperature, and may, therefore, be dismissed at once. Debye's formula and Born and von Karman's formula both give specific heat curves which are very similar to those given by the Nernst-Lindemann formula. All of them give C_v , rather than C_p .

The formula of Debye is

$$C_v = 3R \left\{ \frac{4}{5} \pi^4 \left(\frac{T}{\beta\nu} \right)^3 - \frac{3}{e^{\beta\nu/T} - 1} \right. \\ \left. - 12 \beta\nu/T \sum_{n=1}^{n=\infty} e^{-n\beta\nu/T} \left(\frac{1}{n\beta\nu/T} + \frac{3}{n^2 (\beta\nu/T)^2} + \frac{6}{n^3 (\beta\nu/T)^3} + \frac{6}{n^4 (\beta\nu/T)^4} \right) \right\}.$$

This formula was shown by Debye to give results almost identical with those of the Nernst-Lindemann formula, except at very low temperatures, where it gives higher results. Nernst and Lindemann have carried out the laborious computations necessary to compare the results obtained with this formula and with their own formula with experimental results in the cases of aluminum, copper, silver, diamond, potassium chloride, and sodium chloride. They conclude that the new Debye formula is slightly better than their own. However, a careful examination of the results of these computations shows that the advantage of the Debye formula is very small, if it exists at all. The two formulas agree with each other much better than either agrees with the experimental results, and each has the advantage in about one-half of the cases, and they, therefore, may be regarded as practically identical, until data are available which are accurate enough to make possible a choice between the two formulas.

In the following mathematical development of the theory and the computations based thereon, we have used the Nernst-Lindemann formula in preference to the Debye because of its much simpler mathematical form,

¹ *Ann. Physik.*, **39**, 789 (1912).

² *Physik. Z.*, **13**, 308 (1912).

³ *Z. Elektrochem.*, **19**, 711 (1913).

and because it is the form used by Nernst and his students to test the theory.¹

So many doubtful assumptions are involved in the derivation of the Nernst-Lindemann formula that it seems to us best to regard it simply as an empirical formula, in which the numerical value of a and one or more values of $\beta\nu$ are selected arbitrarily to fit the data as well as possible. There can be no doubt that a polynomial series in powers of T would require many more empirical constants to make it fit the data as well.

By Kirchhoff's Law

$$\frac{dU}{dT} = C_F - C_P = \sum_{F,P} \left\{ \frac{(\beta\nu/T)^2 e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2} + \frac{(\beta\nu/2T)^2 e^{\beta\nu/2T}}{(e^{\beta\nu/2T} - 1)^2} \right\} + \sum_{F,P} aT^{3/2} \quad (1)$$

U is the heat evolved when the reaction proceeds isothermally in such a way that no external work is done. If only solids are involved in the reaction, and the pressure is not over one atmosphere, the external work due to changes in volume during the reaction may be neglected.

C_F and C_P are the heat capacities of the factors and the products of the reaction, respectively, at constant pressure.

Integrating:

$$U = U_0 + \sum_{F,P} \left\{ \frac{\beta\nu}{e^{\beta\nu/T} - 1} + \frac{\beta\nu}{2(e^{\beta\nu/2T} - 1)} \right\} + \sum_{F,P} \frac{2}{5} aT^{5/2} \quad (2)$$

U_0 is an integration constant, but if we place $T = 0$ in this expression, all other terms vanish, and it is, therefore, the heat evolved at absolute zero.

$$A - U = T dA/dT \quad (3)$$

where A is the maximum amount of external work which can be done by the chemical reaction. In the case under consideration, this work is all electrical work.

$$\frac{AdT - TdA}{T^2} = \frac{UdT}{T^2} \quad (4)$$

$$-d\left(\frac{A}{T}\right) = \frac{UdT}{T^2} \quad (5)$$

Before we can integrate, it is necessary to express U as a function of T by means of Equation 2.

$$-d\left(\frac{A}{T}\right) = \frac{U_0 dT}{T^2} + \sum_{F,P} \left\{ \frac{\beta\nu dT}{T^2(e^{\beta\nu/T} - 1)} + \frac{\beta\nu dT}{2T^2(e^{\beta\nu/2T} - 1)} \right\} + \sum_{F,P} \frac{2}{5} aT^{1/2} dT. \quad (6)$$

¹ Nernst has published the calculations with the Debye formula in one case only as far as we have been able to find. Fortunately for our purposes, the case chosen was the formation of silver iodide, in which we are especially interested. This calculation showed that the results for A and U are practically identical, using either the Nernst-Lindemann or the Debye formula. Nernst says "bei der Berechnung chemischer Affinität von kondensierten Systemen sind wohl bei allen Temperaturen (vielleicht ganz extreme Fälle ausgenommen) die Differenzen praktisch belanglos." *Sitzb. Akad. Wiss. Berlin* 1912, 1174.

Integrating

$$-\frac{A}{T} = -\frac{U_0}{T} - I + \frac{3}{2}R \sum_{F-P} \left\{ \frac{\beta\nu}{T} - \ln(e^{\beta\nu/T} - 1) + \frac{\beta\nu}{2T} - \ln(e^{\beta\nu/2T} - 1) \right\} + \sum_{F-P} \frac{4}{15}aT^{5/2}. \quad (7)$$

$$A = U_0 + IT - \frac{3}{2}R \sum_{F-P} \left\{ \frac{3}{2}\beta\nu - T \ln(e^{\beta\nu/T} - 1) - T \ln(e^{\beta\nu/2T} - 1) \right\} - \sum_{F-P} \frac{4}{15}aT^{5/2} \quad (8)$$

Differentiating

$$\frac{dA}{dT} = +I - \frac{3}{2}R \sum_{F-P} \left\{ \frac{3}{2} \frac{\beta\nu}{T} - \ln(e^{\beta\nu/T} - 1) + \frac{\beta\nu/T}{e^{\beta\nu/T} - 1} - \ln(e^{\beta\nu/2T} - 1) + \frac{\beta\nu/2T}{e^{\beta\nu/2T} - 1} \right\} - \sum_{F-P} \frac{2}{3}aT^{3/2}. \quad (9)$$

I is an integration constant, which is thermodynamically indeterminate, and whose physical significance is by no means clear.¹ The presence of this constant in the equation for A and dA/dT makes it impossible to compute the free energy from data on specific heats and thermochemical data alone, but makes it necessary to determine A experimentally for some one temperature at least. This very greatly restricts the usefulness of the equation, because there are many reactions for which the thermochemical and specific data are available or readily obtainable experimentally, whose free energy cannot be determined by any means known to us at the present time.

The two fundamental assumptions made by Nernst, and which constitute the essence of the so-called Nernst Heat Theorem, are

$$\lim_{T=0} \left(\frac{dU}{dT} \right) = 0$$

and

$$\lim_{T=0} \left(\frac{dA}{dT} \right) = 0.$$

These assumptions apply only to reactions taking place in "condensed systems," *i. e.*, in systems involving only solids and liquids, but no gases or solutions. The possible truth of these relationships was clearly foreshadowed by Richards,² but at the time very few data were available on specific heats at low temperatures so that a rigid test of these ideas was impossible. Does the new evidence made available since 1902 en-

¹ Lewis, *THIS JOURNAL*, 35, 29 (1913). Haber "Thermodynamics of Technical Gas Reactions" translation by A. B. Lamb, p. 41ff.

² See especially *Proc. Amer. Acad.*, 38, 302 (1902), and *Z. physik. Chem.*, 42, 138 (1902).

able us to advance beyond the conservative position taken by Richards at that time?

If the specific heats of all solids approach the same limit zero, as we approach absolute zero, as required by the Nernst-Lindemann formula, and as found experimentally in the case of the diamond, then the first assumption follows as a necessary consequence by Kirchhoff's Law.

If in the expression for dA/dT we place $T = 0$, everything vanishes except the term $+I$, leaving $\lim_{T=0} \left(\frac{dA}{dT} \right) = I$.

Therefore, if we accept the Nernst-Lindemann¹ specific heat formula as valid down to absolute zero, then a mathematically equivalent way of stating the second of Nernst's assumptions for condensed systems is $I = 0$. This is very important, if it can be proved, because it makes it possible to calculate, from thermal data alone, the free energy of any reaction, and hence the equilibrium constant of the reaction, and the electromotive force of a galvanic cell. This assumption has been referred to by some of Nernst's disciples² as the Third Law of Thermodynamics. But as the First and Second Laws of Thermodynamics were established only by extensive experimental evidence, similar evidence will be required to justify this title.

Nernst's second assumption may be tested by the data presented in this paper, measurements of the heat capacities of silver, iodine, and silver iodide made by Nernst³ being accepted.

The following table shows the values of $\beta\nu$ and a , which have been selected by Nernst in order to make the results computed with the Nernst-Lindemann formula agree as well as possible with the experimental results.

| | $\beta\nu$. | a . |
|----------|--------------|----------|
| Ag..... | 221 | 0.000048 |
| I..... | 98 | 0.000100 |
| AgI..... | 220 and 70 | 0.00020 |

In the case of silver, the calculated and observed results agree within about 1%. These results are also confirmed, at least down to liquid air temperatures, by the results of Richards and Jackson, and Griffiths and Griffiths within 1%. The results on silver iodide agree with those computed from

¹ The same would be true for any other specific heat formula, which would yield a function in the equation for dA/dT which vanishes when $T = 0$. This would be true for the Debye formula, or for a formula having the form of a convergent polynomial series $C_p = a + bT + cT^2 + \dots$, in which the first term a is zero in accordance with Nernst's first assumption.

² For example, Karl Jellinek, "Physikalische Chemie der homogenen und heterogenen Gasreaktionen unter besonderer Berücksichtigung der Strahlungs- und Quantenlehre sowie des Nernstschen Theorems." (Book published by Hirzel, Leipzig, 1913, p. 478.)

³ *Ann. Physik.*, 36, 395 (1911).

the formula nearly as well. Recently a new series of results on silver iodide has been published by Nernst and Schwes, ¹ using a much modified apparatus. By plotting the new results and the old results (C_p against T) it becomes evident that the new and the old results do not agree well with each other, and moreover the curve depicting the new results has an abnormal and unusual shape. ² Moreover no new results on iodine and silver obtained by the new method are available, and it, therefore, seems best to use the old results in this computation. In the case of iodine, the agreement is not so close, discrepancies of $\pm 3\%$ being common, and at the lowest temperature (28.3°A), the discrepancy is 6% .

Estreicher and Staniewski ³ have measured the average specific heat of iodine from -190° to $+17^\circ$ and from -80° to $+17^\circ$. Their result is 2% higher than that computed from the Nernst-Lindemann equation using the above values of $\beta\nu$ and a .

A plot of these results shows very clearly that the heat capacity of silver iodide exceeds the sum of the heat capacities of silver and iodine.

The best way to test the question whether or not $I = 0$ is to substitute the above values of $\beta\nu$ and a in Equation 9, which gives the following results:

$$\text{at } 0^\circ \text{ } dA/dT = I + 2.18 \text{ calories per degree;}$$

$$\text{at } 25^\circ \text{ } dA/dT = I + 2.20 \text{ calories per degree.}$$

But the value found experimentally with 0.05 N KI solution was

$$dA/dT = 4.52 \text{ calories per degree}$$

$$\text{hence } I = 4.52 - 2.19 = +2.33 \text{ calories per degree.}$$

This may be checked in another way by using Equation 8, which gives the following results:

$$A_{273} = U_0 + I \times 273 + 510 \text{ calories.}$$

$$A_{298} = U_0 + I \times 298 + 565 \text{ calories.}$$

But according to our measurements with 0.05 N solution

$$A_{273} = 15687 \text{ calories.}$$

$$A_{298} = 15800 \text{ calories.}$$

Then solving these two equations simultaneously, we obtain $I = 2.33$ and $U_0 = 14541$, and since $273 \times 2.33 = 636$, the term IT , which Nernst assumes to be zero and discards, is greater than the sum of all the terms involving the $\beta\nu$ and a of the Nernst-Lindemann specific heat formula.

In an exactly similar way we may carry out the computations with our results obtained in 0.1 N solution, for which the experimental value of

¹ *Sitzb. Akad. Wiss. Berlin*, 1913, 367.

² The increase in C_p with the temperature is very great up to 85.2°A , and then becomes unusually small, giving a sharp bend in the curve which is abnormal. The curve for the old results has the shape commonly found in such curves.

³ *Bull. Akad. Cracovie*, 1912, 834.

$dA/dT = 3.679$, which gives $I = 1.50$, and $U_0 = 14800$. This, however, is believed to be less reliable than the results with the more dilute solution. It should be noticed that the more dilute solution, in which the activity of the ions is more nearly proportional to the concentration, shows the higher value of I .

A quite different procedure is sometimes adopted in papers from Nernst's laboratory to prove that $I = 0$. Equation 8 is used (with the term IT missing, which, of course, involves the assumption that $I = 0$), to calculate a numerical value of U_0 from the experimentally determined value of A at one temperature. Then, using this value of U_0 , the numerical value of U is computed by means of Equation 2, and this value is compared with the experimentally determined value of U . But since the exact value of U is often in doubt by many hundred calories a rigid test of the fundamental assumption is not secured. Or the procedure may be reversed by calculating U_0 from U by Equation 2 and then calculating A from Equation 8 (with the term IT missing). In either case the uncertainty in U makes a rigid test impossible.

An examination of Equation 9 shows that U_0 has been eliminated and that, therefore, what is really needed to secure a more direct determination of the value of I is a determination of the temperature coefficient of the free energy. Since electromotive force measurements are, in general, more precise than calorimetric measurements, and since in a comparison of very similar measurements made at slightly different temperatures, systematic errors are largely eliminated, unless these errors have an appreciable temperature coefficient, we conclude that the value of I can best be determined by means of data on the temperature coefficient of the electromotive force of galvanic cells. It is obvious from Equation 9 that an accurate determination of the temperature coefficient is of primary importance in testing the Nernst Heat Theorem.

There still remains the possibility that I might be made equal to zero by a slight change in $\beta\nu$ and a , which would still give calculated values for the specific heats which were within the limit of accuracy of the experimental determinations of specific heats.

In order to test this possibility we assume the $\beta\nu$ and a values for silver and silver iodide to be correct, because these agree with the formula best, and find by trial that, if we assume for iodine $\beta\nu = 143$ and $a = 0.00007$, then the computed value of dA/dT becomes $+4.5$, which makes $I = 0$. Then we compute the atomic heat capacity of iodine from these values, which shows that the computed results differ from the observed by an amount which is many times the experimental error. For example, at 28.3°A , the computed value is 2.31 calories per degree, whereas the observed value is 3.78, at 36.5° , the computed value is 3.14, and the observed

4.17; at 77°, the computed value is 5.07, and the observed value 5.38; at 298° the computed value is 6.21 and the observed 6.64.

We, therefore, conclude that in the present state of our knowledge the variation of heat capacity with the temperature and with the available data on the heat capacities of the substances concerned, the evidence of the case is against the general theorem that $I = 0$ in the case of all reactions between solids.

While the experimental work described in this paper was in progress, there appeared a paper by Ulrich Fischer,¹ describing an experimental study of the same problem, as it was carried out in Nernst's laboratory. Fischer interprets his results as supporting the Nernst Heat Theorem. He found $dA/dT = 2.419$ calories per degree from his cells containing 0.5 *N* KI, $dA/dT = 1.267$ from cells containing $1/3$ *N* KI, and $dA/dT = 1.66$ from cells containing 0.1 *N* KI.

Fischer reports measurements on seven cells containing 0.1 *N* KI at temperatures ranging from 14.2 to 40.2°, the results being best expressed by the equation, $E = 0.6916 + 0.000305 t$.

Fischer's cells were, however, less satisfactory than ours in constancy and reproducibility, the average difference of his 35 measurements from the mean expressed by the above equation being 0.9 millivolts, with a maximum difference of 2.8 millivolts, and 6 out of the 35 readings showing a difference of 2 millivolts or more. Our cells showed variations not more than 0.1 of this, and were about 1 millivolt higher. His cells containing 0.5 *N* KI are even less reproducible, the average deviation from the mean being 1.15 millivolts, and the maximum 5.7 millivolts. Our experience leads us to infer that the cause of this irregularity in Fischer's cells was in the liquid junction. We constructed some cells like Fischer's, and found them not to be reproducible with an accuracy better than 1 millivolt.

Fischer makes no reference to the potential at the boundary of the two solutions, which has a value of about +3.0 millivolts at 0°, and +3.2 millivolts at 25°, thus raising the value of dA/dT .

In applying a correction for osmotic work, Fischer makes an error which makes his value of dA/dT less than it ought to be. He assumes that all the iodine dissolved in potassium iodide solution is present as KI_3 . But, in the stronger solutions ($N/3$ and $N/2$) the existence of higher complexes and the deviations of these solutions from the laws of dilute solutions cannot be safely ignored. Furthermore, an appreciable part of the free iodine is present as I_2 , especially in the 0.1 *N* solution, and, moreover, the amount present as I_2 increases greatly with the tempera-

¹ *Z. anorg. Chem.*, 78, 41 (1912).

ture,¹ so that their neglect of this fact results in an error in their value for the temperature coefficient, dA/dT .

In order to apply this correction accurately, and to make the application of the liquid junction correction possible, a careful study of the conditions in solution of KI saturated with iodine at 13.1°, 23.9° and 35.4° should have been made by Fischer, similar to the work of Bray and Mackay at 25°, and Jones and Hartmann at 0°. An estimate based on these two investigations indicates very clearly that Fischer's rough method of applying the correction has made his temperature coefficient less than one-half of what it should be. In the discussion of Equations 8 and 9, it was pointed out that accuracy in the determination of the temperature coefficient is essential to make a test of the Nernst Heat Theorem of any value.

Summary.

The electromotive force of silver-silver iodide-iodine cells was measured at 0° and 25°.

An improved method of preparing silver-silver iodide electrodes was devised.

An improvement in the constancy and reproducibility of the results was secured when the junction between the solutions around the electrodes was made to occur within a ground-glass joint.

The free energy of formation of silver iodide from silver and iodine is 65.1 kilojoules at 0°, and 66.1 kilojoules at 25°.

These measurements show that the affinity of silver and iodine for each other increases with rising temperature, which makes possible a plausible explanation of the negative coefficient of expansion of silver iodide, and thus supports the analysis of coefficients of expansion based on the Richards' hypothesis of compressible atoms.

The heat of formation of silver iodide is 61.0 kilojoules.

It is shown that the relationships between the properties and thermodynamic constants of silver iodide support many conclusions which Richards drew from his hypothesis of compressible atoms, but that they do not support the second of the assumptions which Nernst applied to these conclusions, commonly known as the Nernst Heat Theorem.

It is shown that the best way to test the Nernst assumptions is by means of accurate determinations of the temperature coefficient of free energy, interpreted by Equation 9.

CAMBRIDGE, MASS.

¹ The solubility of iodine in pure water in mols I₂ per liter is

| | | | |
|-----|---------------------------------|-----|------------------------------|
| 0° | 0.000638 Jones and Hartmann | 35° | 0.00184 Hartley and Campbell |
| 18° | 0.000709 Hartley and Campbell | 45° | 0.00255 Hartley and Campbell |
| 25° | 0.00134 Noyes and Seidensticker | 55° | 0.00303 Hartley and Campbell |
| | Sammet, Hartley and Campbell, | 60° | 0.00416 Sammet |

Bray.

RADIOMETRIC MEASUREMENTS OF THE IONIZATION CONSTANTS OF INDICATORS.¹

By E. J. SHAEFFER, M. G. PAULUS AND HARRY C. JONES.

Received February 22, 1915.

The radiometric measurements recorded in this paper were made with a very sensitive radiomicrometer and a grating spectroscope. The spectroscope is well known to the chemist, but its use in connection with the radiomicrometer, has not, as yet, found an extensive application to the study of chemical problems. This is perhaps due in part to the difficulty in constructing a sensitive and easily controlled radiomicrometer. By means of the grating spectroscope and radiomicrometer, it is possible to study quantitatively chemical reactions involving color changes, and even those not involving such changes, if there are absorption bands in the invisible regions of the spectrum. It will be seen that accurate determinations of very small concentrations of colored components in solutions, can be made very rapidly even when two or more such components are present. The structure of the solvent bands, and time reactions, are a few of the many other important chemical problems which may be investigated by means of this radiometric apparatus.

Purpose of this Investigation.—In connection with some problems now under investigation in this laboratory, it was desired to secure accurate measurements of the hydrolysis constants of certain salts. The spectroscope and radiomicrometer suggested the indicator method, which is based on the changes in the transmission of light by solutions of indicators when varying amounts of hydrogen or hydroxyl ion are present. It will be shown that by means of these changes the concentrations of very small amounts of hydrogen and hydroxyl ions can be determined. The method obviously involves a knowledge of the ionization constant of the indicator as an acid or as a base. A comparison of the ionization constants of the indicators obtained by several investigators, showed that the recorded values varied widely, not only with different methods, but with the same method. The results for phenolphthalein in particular, show how inaccurate is our knowledge concerning the ionization constant of that important indicator. Salm² gives the value 8×10^{-10} ; McCoy,³ 0.8×10^{-10} . In many cases the results of an individual investigation vary as much as 300 to 400 per cent. A. A. Noyes⁴ has applied the theory of indicators to volumetric analysis, making use of the ionization constants of the various indicators. He expresses the opinion that our knowledge of the ionization constants of the indicators is for the most part inexact,

¹ This investigation was carried out with the aid of a Grant from the Carnegie Institution of Washington generously awarded to H. C. Jones.

² *Z. phys. Chem.*, **57**, 492 (1907).

³ *Am. Chem. J.*, **31**, 503 (1904).

⁴ *THIS JOURNAL*, **32**, 858 (1910).

and needs to be supplemented by further careful investigation. Stieglitz,¹ McCoy,² and Salm² have also recognized the importance of such a study. McCoy, Salm, and in particular Noyes and Bjerrum,³ have already applied the indicator constants to some of the more important problems which the chemist must face in titrating weak acids and bases; and they have shown in certain cases the extent of the error involved in such titrations. It will then be readily seen, that it is important to know the ionization constants of the more important indicators, especially of methyl orange and phenolphthalein. In view of these facts, and the value of such ionization constants in many other lines of work involving the use of indicators, it was decided to make a radiometric investigation of this problem. Methyl orange was first studied, and a method was developed through the application of Beer's law, which readily gave the concentration of the yellow azo-base and that of the red quinoid ion. Knowing these values and the hydrogen ion concentration, the hydrolysis constant of methyl orange can be readily calculated. The method employed is different from, and was worked out independently of any other method thus far used in investigating this problem.

Historical.—The results of a number of preliminary investigations on the ionization constants of various indicators were published in 1904. McCoy,⁴ like most of the other investigators who studied this problem, worked colorimetrically, the intensity of the color being judged by the eye. McCoy employed Nessler tubes for this purpose, while others made use of special colorimeters to determine the amount of indicator transformed into its salt by varying amounts of hydrogen or hydroxyl ions. Tables showing roughly the hydrogen ion concentration at which a large number of indicators undergo change in color, have been published by Friedenthal,⁵ Salessky,⁶ Fels,⁷ and Salm.⁸ Nearly all of the early investigators utilized the principle that the ionization constant of an indicator is equal to the hydrogen ion concentration at which it is one-half transformed into its salt. (See Salm² and A. A. Noyes.²) Salessky, and later Salm, determined the concentration of the hydrogen ions at this point by means of the hydrogen electrode. Criticisms showing how inexact most of these methods are will be found in the separate articles. Salm,⁹ referring to the work previous to 1907, says that the investigations have been for the most

¹ THIS JOURNAL, 25, 1126 (1903).

² *Loc. cit.*

³ *Ahr. Versamm.*, 21, 1 (1914).

⁴ *Am. Chem. J.*, 31, 503 (1904).

⁵ *Z. Elektrochem.*, 10, 113 (1904).

⁶ *Ibid.*, 10, 204 (1904).

⁷ *Ibid.*, 10, 208 (1904).

⁸ *Ibid.*, 10, 344 (1904).

⁹ *Z. physik. Chem.*, 57, 490 (1907).

part qualitative, and that with few exceptions, the dissociation constants of the indicators are still unknown. Salm made a more careful investigation, employing a satisfactory colorimeter to determine when the indicator was one-half transformed into its salt, and like Salessky obtained the hydrogen ion concentration at this point by means of the hydrogen electrode. The results which he obtained with phenolphthalein illustrate the uncertainty of the values found by his method. Wegscheider¹ proceeded in much the same manner as the others who have used the colorimetric method, and obtained constants for the ionization of phenolphthalein which seem to be in fair agreement with those found by Hildebrand.² Hildebrand's method, involving the use of the spectro-photometer for the estimation of color intensities, is the most exact of all the methods previously employed. His photometric method somewhat resembles the radiometric method which we employed. Rosenstein,³ following essentially the procedure of McCoy, has carried out very carefully a colorimetric investigation of the ionization constant of phenolphthalein, and the effect upon it of neutral salts. He employed the Duboscq type of colorimeter to determine the fraction of the indicator transformed by a known hydrogen ion concentration. As he shows, the ionization constant is equal to the hydrogen ion concentration, times the fraction of the indicator transformed into its salt. When the indicator is a fairly strong electrolyte, *e. g.*, *p*-nitrophenol, its dissociation constant was determined by the conductivity method.

Before we can judge of the absolute value of the results obtained in any radiometric investigation, it is necessary that the radiometric instrument, and the other parts of the apparatus used in connection with it, fulfill several requirements. What these requirements are will be taken up in the discussion of the apparatus which follows. In view of the fact that radiometric apparatus has not been extensively used by chemists, it seems desirable that this be discussed in some detail.

The Radiomicrometer.—The methods employed in the construction of the radiomicrometer and especially of the thermo-junctions, we owe to Prof. A. H. Pfund.⁴ By means of these methods we were able to build a very satisfactory instrument.

The radiomicrometer previously constructed by Guy⁵ was found to be unsatisfactory for use with the grating spectroscope. Its sensibility, according to a recent test, was 2 per sq. mm. of exposed vane, candle and scale being at a meter's distance. The full period of this instrument was,

¹ *Z. Electrochem.*, 14, 510 (1908).

² *Ibid.*, 14, 351 (1908).

³ *THIS JOURNAL*, 34, 1117 (1912).

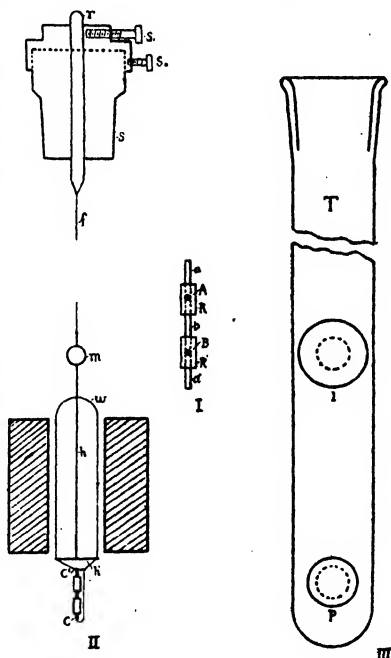
⁴ *Phys. Rev.*, 34, 228 (1912); *Phys. Zeit.*, 13, 870 (1912).

⁵ Publication of the Carnegie Institution of Washington, No. 190, 30 (1913).

however, very short, it being 8 seconds. His radiomicrometer could have been made about as sensitive as the one constructed for this work, by using a longer and finer quartz fiber, and making the full period about 20 seconds. However, due to the fact that this instrument was not equipped with a compensating junction, and that its drift, due to this cause, had proved so troublesome in the work of the previous year, it was decided to construct a new radiomicrometer.

Briefly, the radiomicrometer consists of a thermo-electric junction attached to a loop of nonmagnetic wire. The whole system is suspended by a quartz fiber in a glass tube. A strong magnetic field surrounds that portion of the tube inclosing the loop of wire. Radiant energy falling upon the blackened junction is converted into electrical energy. In proportion to the amount of energy received by the junction, the suspended system turns through a definite angle in the magnetic field, the loop tending to set itself at right angles to the lines of force. The deflection or turn is given by means of a mirror attached to the suspended system.

The essential parts of the radiomicrometer are shown in the following sketch. Fig. I represents the type of compensating junction which was constructed and used. It is fastened to the loop of copper wire w at c and c' , as shown in Fig. II. To support the loop of wire small glass rods are placed at h and h' . A light mirror is attached to h at m . A quartz fiber, f , is fastened to the end of the glass rod h , and to the brass stopper S . The whole system is then set in the glass tube T , having two windows l and p . The lens l focuses the reflected light from the mirror m , on a glass scale. At p is inserted a plane glass window i mm. thick. The beam of light which is to be measured passes through this window before falling on the junction. The magnetic field is placed between l and p .



The wire loop was made of a very fine specimen of No. 36 copper wire, furnished by Leeds and Northrup. Pure nitric acid was used to dissolve the exterior surface of the wire, which was very likely to be contaminated with various magnetic materials. That this wire must have been very pure is shown by the behavior of the completed instrument. As regards purity,

a still better specimen of silver wire was obtained from Weston; but unfortunately none of the junctions attached to this silver wire were sufficiently sensitive for our purpose.

The alloys used for the construction of the thermo-junction were of the composition recommended by Hutchins.¹ Fig. I of the sketch gives an enlarged view of the junction. It will be noticed that it consists of two thermo-electric junctions A and B, which compensate each other. When the same beam of light falls on both junctions, each sends equal amounts of electrical energy through the loop of nonmagnetic wire w , but in opposite directions. Hence, it follows that for exact compensation there should be no turn of the suspended system. In actual operation the beam of light energy which is to be measured is focused on one of the junctions. This arrangement of junctions is quite essential in any sensitive radiomicrometer where a constant zero point is required; and it is only in this way that the effects of temperature changes and stray sources of light can be eliminated.

The two arms represented by a and a' in Fig. I, have the composition 97 parts bismuth and 3 parts antimony. The composition of b is 95 parts bismuth and 5 parts tin. These metals are quite pure and the strips used are very thin. Junction A is formed by sealing strip a to strip b , and junction B is formed by sealing strip b to strip a' . R. and R' are the receiving surfaces, or so-called vanes, cut from very thin tin foil, and soldered to junctions A and B, respectively. These vanes each have an area of four square millimeters, and are coated with lamp black to prevent radiation of light energy. It was found that the action of an acidified solution of antimony chloride on the tin foil produces a black receiving surface. Theoretically, it appears that such a metallic receiving surface should be more effective than lamp black. However, none of the junctions having the antimony receiving surface were sufficiently sensitive to determine whether or not its use is to be preferred to that of lamp black. Greater sensibility can be obtained with a single junction than with a compensating one, since in the former we have but one seal and two metal strips. This follows from the fact that the sensibility of the radiomicrometer is materially increased when the resistance of the junction is made more nearly equal to that of the wire loop. However, the advantages to be derived from the compensating type of junction are well worth the sacrifice in sensibility.

It is very important that the weight of the junction be kept as small as possible, not only to lessen the weight of the suspended system, but especially to reduce the heat capacity of the junction to a minimum. A small heat capacity insures a quick acting suspension, and one which will more rapidly return to the zero point. That the mass of material

¹ *Sill. Journ.*, 48, 226 (1894).

in the junction is very small, can be seen from the fact that the actual weight of one of the completed compensating junctions was 2.9 milligrams.

The quartz fiber¹ was obtained from molten quartz by means of a bow and arrow arrangement. The total length of this fiber is nearly 30 cm. A long fiber materially aids in eliminating vibrations. This is most essential, especially when the work necessitates small deflections. The period and sensibility of the radiomicrometer depend in a large measure on the proper selection of the quartz fiber.

The plane mirror *m* (Fig. II) is very thin and has an area of about 20 sq. mm. Directly in front of it is the lens *l*, having a focal length of twelve feet. By means of this arrangement the image of a lamp filament could be sharply focused on a glass scale about twelve feet distant from the mirror; and it is on this scale that the deflections as given by the radiomicrometer are noted.

The torsion-head stopper *s*, made of brass and tightly ground into the glass tube *T*, serves the purpose of making adjustment. By means of it, the suspended system can be made to occupy any position in the magnetic field, and the whole system can be raised or lowered without danger of breaking the very fragile suspension. The torsion-head stopper contains a brass rod *r* and the two screws *s_i* and *s_{ii}* for making the above adjustments.

The glass tube *T* in which the whole system is suspended is about 45 cm. in length. To it is attached the lens *l* previously referred to, and the glass window *p*, through which the beam of light is directed either to junction *A* or to junction *B*.

The glass tube surrounding that portion of the suspended system to which the thermo-junction is attached was insulated from temperature changes and air drafts by a layer of fine lead shot and wool fiber. To prevent stray sources of light and air drafts from reaching the radiomicrometer, it was inclosed in a wooden box covered with painted canvas.

That the image on the scale should remain steady at a focal distance of twelve feet, it is necessary to shield the radiomicrometer very carefully from the usual vibrations of the building. The long quartz fiber aided materially in this respect. Between the leveling stand of the radiomicrometer and the base on which it rested, various insulating materials were introduced at six points to absorb vibrations.

The completed radiomicrometer, candle and scale being at a meter's distance, gave a deflection of 20 cm., the half-period being nearly 10 seconds. In making this determination of the sensibility of the instrument the radiation was passed through a glass window 1 mm. thick, and the tube containing the suspension was not evacuated. Evacuating the tube and passing the radiation through a rock salt window would increase the sensibility about six times, and the period would become somewhat shorter.

¹ Dr. C. W. Hewlett has very kindly supplied us with several satisfactory fibers.

Since the receiving vane has an area of four square millimeters, the sensibility per square millimeter of exposed vane is 5, and the full period 20 seconds. When making this determination, owing to the difficulty of properly shielding the junction not in use but serving as compensator, it is thought that the value of 5 for the sensibility is somewhat low. Practically every junction that was tested showed that the sensibility was approximately one-fourth of the whole period in seconds. The sensibility value as given by the candle has but little meaning, owing to the varying intensity of the light emitted. The light from the Nernst glower burning at 0.8 ampere and 120 volts, dispersed into the visible first order spectrum six inches long at slit s_1 of the spectroscope, gave at $\lambda = 0.95\mu$, a deflection of 250 mm. when focused on the junction of the radiomicrometer. Both slits are 1 mm. in width, and the scale twelve feet from the mirror. Considering the high resolving power of the grating, it will be seen that our radiomicrometer is very satisfactory both as regards sensibility and period. It enabled us to make quantitative measurements of radiant energy from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$.

For the same source of light energy, the radiomicrometer always gave the same deflection and returned quickly to zero; showing that our efforts to eliminate magnetic materials from the wire loop had been very successful. The conduct of the completed instrument has demonstrated that the suspended system is very free from paramagnetic disturbances. The diamagnetic materials composing the junction were all arranged at right angles to the lines of force of the magnetic field, and in this way diamagnetic disturbances were reduced to a minimum. The use of the radiomicrometer has shown that the heat capacity of the junction is sufficiently low to be within the desired limit. The compensating junction and its insulation from temperature changes practically removed any drift of the zero point. The zero point for weeks at a time would not drift more than 10 cm. on either side of the zero. In case there was any drift during the measurements, it was always very slight and the proper correction could easily be applied. The insulation from vibrations made the reflected beam upon the scale fairly steady, even when there were rather violent disturbances in the building. There is every reason to suppose that the scale could be read to about one-quarter of a millimeter when the building was quiet. Duplicate readings under ordinary conditions nearly always agreed to within 0.5 mm.

The Spectroscope.—The grating spectroscope was designed and built in the Physical Laboratory under the direction of Prof. John A. Anderson. The use of such a spectroscope presents two especially desirable advantages. First, the position of regions of absorption can be very accurately determined; second, due to its high resolving power, the structure of even the very narrow absorption bands and some absorption lines can be

studied in detail. The spectroscope is so constructed that either the photographic plate or any of the radiometric instruments can be used with it. The use of the radiomicrometer enables us to determine not only the actual positions of regions of absorption, but also to make quantitative measurements of the light transmitted by a solution, for a wide range of wave lengths. The deflections of the radiomicrometer give an accurate measure of the relative intensities of the different absorption bands, and of the different parts of the same bands. It will thus be seen that the radiometric method has distinct advantages over the photographic method, which is chiefly useful in determining the positions of regions of absorption and the general characteristics of the visible spectrum as transmitted by the solutions. Moreover, the photographic plate is only sensitive from $\lambda = 0.2\mu$ to $\lambda = 0.76\mu$, whereas, with the radiomicrometer and the apparatus used in this work, quantitative measurements of absorption could be made from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$, using slits only 1 mm. in width. Considering the high dispersion that could be obtained with the four inch grating, this width of slit gives a very pure spectrum.

The plane four inch grating with which the spectroscope is equipped, was ruled by Anderson; and the ruling is of such a character that a very bright first order spectrum is produced. This is quite essential for radiometric measurements in the visible region of the spectrum. Energy measurements were made in both first order spectra, one being on each side of the central image. The spectrum on one side was found to be somewhat more intense, and therefore this brighter side was used.

If either the intensity of the light source, or the sensitiveness of the radiomicrometer exceeds certain limits, it is possible that light energy from the second order spectrum will vitiate the energy measurements made in the first order spectrum. This will be readily seen if we consider that wave length of light $\lambda = 0.35\mu$ of the second order overlaps wave length of light $\lambda = 0.7\mu$ of the first order, etc. Therefore, it was desired to know if, with a Nernst glower burning at 0.8 amperes and 120 volts, the second order spectrum had sufficient energy to be detected by the radiomicrometer. If such proved to be the case, it would be found necessary to introduce color screens to eliminate the light energy from the second order spectrum. That the first order spectrum can be regarded as pure is shown by the following considerations.

Glass cuts off all wave lengths of light beyond $\lambda = 0.35\mu$. Since the glass in the path of the light is of considerable thickness, the first order spectrum is not contaminated with any light from the second order spectrum as far out as $\lambda = 0.7\mu$ of the first order. A solution of copper sulfate is entirely transparent to all wave lengths of light shorter than $\lambda = 0.6\mu$. A 10 mm. depth of a saturated solution of copper sulfate shows complete absorption beyond $\lambda = 0.6\mu$. Using the above solution

of copper sulfate, radiometric measurements were made from $\lambda = 0.4\mu$ to $\lambda = 1.3\mu$. Beyond $\lambda = 0.6\mu$ the solution of copper sulfate is entirely opaque, and therefore no evidence of light energy from the second order was obtained as far out as $\lambda = 1.3\mu$. It has already been shown that the first order spectrum is pure up to $\lambda = 0.7\mu$, and the above shows that the light from the overlapping second order spectrum does not contain a sufficient amount of energy to be detected by the radiomicrometer as far out in the infra-red as $\lambda = 1.2\mu$ of the first order spectrum. The radiometric measurements of the dissociation constants of the indicators were all made between $\lambda = 0.5\mu$ and $\lambda = 0.6\mu$, and in this region the first order spectrum is absolutely pure.

The drum head which rotated the grating through definite angles is a large one, its diameter being four inches. It is attached to a very carefully constructed screw, so designed that each complete revolution changes the wave length of light falling on the slit by approximately 500 Ångstrom units. The drum contains five hundred divisions, and, all things considered, it is quite probable that the wave length settings are accurate to within one or two Ångstrom units.

The spectroscope is of the Littrow mounting, the same lens serving both as telescope and collimator. It is provided with two four inch lenses made by Brashear. One lens has a focal length of 72 inches and is intended for photographic work. The other, and the one which was used in this work, has a focal length of 30 inches. With this lens, the visible first order spectrum at slit s_2 , has a length of over six inches. Provision has also been made for the mounting of a large glass prism on the grating table, and it is purposed to use this prism when an intense first order spectrum is desired, rather than a spectrum which is widely dispersed. Had we not been successful in constructing a very sensitive radiomicrometer, it would have been necessary to make frequent use of the glass prism.

The spectroscope was placed in a brass box, blackened on the inside, which prevented stray sources of light from reaching the grating. The slits were of the bilateral type.

The calibration curve for the grating and drum head was calculated from the known grating space, by means of the equation:

$$\lambda = 33,866.7 \sin \frac{3000T + 6R}{3500}$$

where T is the number of complete turns of the screw which rotates the grating, and R is the reading on the drum. The calibration was also effected by observing the positions of various mercury, sodium and lithium lines. It was decided that the calculated values are more accurate than the observed; and, accordingly, the dispersion curve based on the calculated values was used.

Source of Light.—A Nernst glower served as the source of light, the electrical energy being supplied by a series of storage batteries. By means of a rheostat, the light intensity could be kept quite uniform. The glower was protected from air drafts by means of a box of asbestos wood. Provision was also made for the mounting of a nitrogen lamp,¹ when it was desired to secure large deflections of the radiomicrometer for wave lengths of light shorter than $\lambda = 0.5\mu$.

The Cells.—A very important part of the equipment is the cells which contain the solutions to be investigated. There are two cells both made as nearly alike as possible. The cell consists of two brass cylinders which closely telescope into one another. One end of each cylinder is closed by a glass plate held in position by Wood's fusible metal. The four glass ends used in the cells are all of the same thickness, *i. e.*, 2 mm. Their surfaces are plane, and are parallel to within five wave lengths of light. It is a difficult problem to set these plates in the brass cylinder with Wood's fusible metal, without warping them and destroying their plane-parallelism. The character of the interference fringes which the plates gave with the mercury arc determined when they were correctly adjusted. A fine thread was "chased" on the outer cylinder. This thread carried a nut which, when turned, raised or lowered the inner cylinder a definite amount. Each complete revolution of this nut changed the distance between the plates by 1 mm. The nut contained 100 divisions, and by means of this arrangement we could readily adjust the depth of the solutions to within less than 0.01 mm. Each cell was then filled with a layer of water 5 mm. in depth, and the deflections given by the radiomicrometer were noted for a light source of uniform intensity throughout the whole region of the spectrum under investigation, namely, from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$. The deflections should agree with each other very closely for all wave lengths of light, if the cells are optically identical. Having made sure that the cells are optically identical, they were heavily plated with gold to remove any possibility of the solutions attacking the metals of the cell. It is very important to keep the solutions perfectly clear when measurements are being made, and the glass ends must be maintained absolutely clean. The following table shows the optical identity of the two cells. Under Cell A and Cell B are given the actual radiomicrometer deflections for various wave lengths of light (Table I).

Having discussed the principal parts of the apparatus, *viz.*, the radiomicrometer, spectroscope, source of light, and the cells; and having shown how they meet the requirements demanded by work of this character, it is desirable to consider next the general arrangement of the various parts.

¹ Dr. W. R. Whitney of the General Electric Co. very kindly supplied us with two lamps of special design to be used for this purpose.

TABLE I.

| $\lambda = \text{\AA. U.}$ | Cell A. | Cell B. | $\lambda = \text{\AA. U.}$ | Cell A. | Cell B. |
|----------------------------|---------|---------|----------------------------|---------|---------|
| 4546 | 4 | 4 | 8029 | 125.0 | 125.0 |
| 4797 | 8.2 | 8.2 | 8275 | 127.0 | 127.5 |
| 5047 | 14.2 | 14.5 | 8520 | 129.0 | 129.0 |
| 5298 | 22.0 | 22.5 | 9009 | 129.5 | 130.0 |
| 5548 | 31.5 | 31.5 | 9497 | 115.5 | 115.0 |
| 5797 | 41.5 | 41.7 | 9982 | 105.5 | 106.0 |
| 6046 | 50.5 | 50.5 | 10465 | 113.5 | 114.0 |
| 6295 | 60.7 | 60.5 | 10946 | 108.5 | 108.0 |
| 6543 | 70.5 | 71.2 | 11424 | 69.0 | 69.0 |
| 6792 | 86.7 | 86.5 | 11900 | 51.5 | 52.0 |
| 7041 | 100.5 | 100.0 | 12373 | 56.0 | 56.0 |
| 7290 | 107.7 | 107.7 | 12843 | 53.5 | 54.0 |
| 7536 | 114.0 | 114.5 | 13314 | 34.0 | 34.0 |
| 7784 | 120.5 | 120.5 | 13775 | 11.0 | 10.7 |

Arrangement of Apparatus.—The Nernst glower, lenses, prisms and carriage for the cells were mounted on an upright steel standard placed by the side and near the end of the spectroscope next to the radiomicrometer. Parallel light from the Nernst glower was made to pass, by means of a carefully adjusted sliding carriage, first through one cell and then through the other. The two cells could thus be made to occupy the same position in the path of the light. The light transmitted by the solutions contained in the cells was then deflected by means of a right angle prism and focused on the slit of the spectroscope s_1 . Inside of the box inclosing the spectroscope and directly in the rear of slit s_1 , was placed another right angle prism which reflected the light through a four inch lens to the grating. The dispersed light was reflected back through this same lens and focused on the slit of the spectroscope s_2 . The light which emerged through slit s_2 was again brought to a focus on the junction of the radiomicrometer. By turning the drum head of the spectroscope to the proper points, we could then determine quantitatively the light transmitted by any solution for all wave lengths of light between $\lambda = 0.4\mu$ and $\lambda = 2.0\mu$.

The Differential Method.—It was desired to measure the absolute percentage transmission of 20 mm. of solution. This was done by a differential method which eliminated corrections for reflection from the glass ends, and differences in the refractive index of the glass and the solutions. The method of procedure is as follows: Cell A is filled with 21 mm. of solution; cell B with 1 mm. of solution. Light of unvarying intensity I_0 , was then passed through cell A, and the intensity of the transmitted light I_I measured by means of the radiomicrometer. As soon as possible cell B was made to occupy the same position formerly occupied by cell A, and the intensity of its transmitted light I_{II} determined. The deflection produced when cell A was in the path of light, divided by that given when cell B occupied the same position, determines the ab-

solute percentage transmission for 20 mm. of solution; or, in other words, I_I/I_{II} is the value desired. The justification for this procedure is seen from what follows.

If the depth of solution under investigation is l , the intensity of the incident light I_0 , and that of the transmitted light I , we have the following relations for depths of solution l' and l'' .

$$I_I = I_0 e^{-kl'} \quad (a)$$

$$I_{II} = I_0 e^{-kl''} \quad (b)$$

Dividing a by b we get

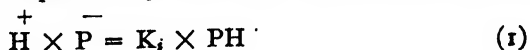
$$I_I/I_{II} = e^{k(l''-l')} \quad (c)$$

But the actual percentage transmission of the same solution of depth $l' - l'' = l$ is given by

$$I/I_0 = e^{-k(l'-l'')} = e^{-k(l''-l')}, \text{ or } I_I/I_{II} = I/I_0. \quad (d)$$

Theoretical Discussion.—The Ostwald¹ theory of indicators, explaining first the cause of color, and second, the difference in sensitiveness of various indicators towards different acids and bases, has been found to be inadequate. Concerning the latter, which is by far the most important side of the indicator question, the Ostwald interpretation is substantially correct. But in consideration of well known relations between the color and structure of organic compounds, and of the researches of Bernthsen,² Nietzi and Burckhart,³ Hantzsch⁴ and others, it has been found necessary to modify the Ostwald view as to the cause of color. The facts and relations brought out by these investigations have been correlated and interpreted by Stieglitz⁵ in the so-called chromophoric theory of color. A. A. Noyes,⁶ in a quantitative application of the theory of indicators to volumetric analysis, has also fully explained the significance of the chromophoric theory. According to this theory it is necessary to consider an indicator solution as containing a mixture of two tautomeric substances of different structural types. The ionization constants of the two forms and the equilibrium relations between them are such that when the indicator exists as a slightly ionized acid or base, one form is present in greatly predominating quantity. The other form largely predominates when the indicator exists as a highly ionized salt.

Considering phenolphthalein, the ionization constant K_i , according to the Ostwald conception is expressed by the simple equilibrium equation:



¹ *Lehrbuch der all. Chem.*, 1, 799 (1891).

² *Chem. Zeit.*, 1956 (1892); also Friedländer, *Ber.*, 26, 172, 2258 (1893).

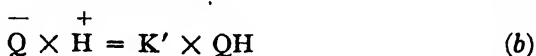
³ *Ber.*, 30, 175 (1897).

⁴ *Ibid.*, 32, 583, 3085 (1899).

⁵ *THIS JOURNAL*, 25, 1112 (1903).

⁶ *Ibid.*, 32, 815 (1910).

The chromophoric theory, as Stieglitz¹ has shown, requires two such equations, (a) and (b).

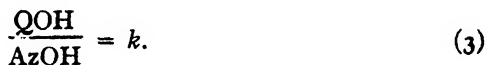


where k is the stability constant expressing the equilibrium relation between the two tautomeric acids. The acid represented by LH is assumed to be a pseudo- or an extremely weak acid; and that by QH is the true acid. Its ionization constant K' is of such a magnitude that the quinoid salt is formed in greatly predominating quantity in the presence of alkalis, the stability constant k acting so as to maintain the equilibrium relation between the two tautomeric acids. The ionization constant for phenolphthalein is the product of the stability constant k , and the ionization constant K' of the acid QH; or combining a and b and incorporating k and K' into K , we have:

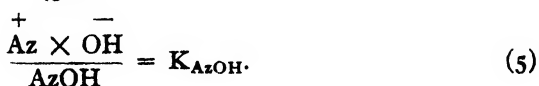


The above equations illustrate the fundamental differences between the two color theories; and accepting the Stieglitz interpretation of K_i according to Equation 2, the theory underlying the calculation of the dissociation constant of methyl orange from radiometric measurements will be discussed.

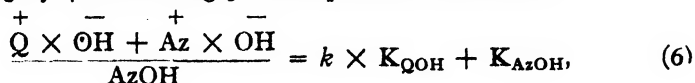
Methyl orange is in reality a weak base. Noyes² has deduced a general expression for the equilibrium relations of any pair of tautomeric bases and their ions. This deduction involves three fundamental equations. Expressing the equilibrium relation k , between the quinoid and azo-base, it being understood that the symbols represent gram-molecular or gram-ionic concentrations, we have:



The quinoid base and the azo-base are also in equilibrium with their ions according to 4 and 5 —



Multiplying 3 by 4 and adding 5 to the product, we obtain:



¹ *Loc. cit.*

² THIS JOURNAL, 32, 818 (1910).

and substituting in the denominator for AzOH its value $\frac{AzOH + QOH}{1 + k}$, it follows that—

$$\frac{Q \times OH + Az \times OH}{AzOH + QOH} = \frac{k \times K_{QOH} + K_{AzOH}}{1 + k} \quad (7)$$

Letting the above equal K_i , we have:

$$\frac{OH(Az + Q)}{AzOH + QOH} = K_i \quad (8)$$

Noyes has called attention to the fact that for a satisfactory two-color indicator such as methyl orange, the sum of the two tautomeric bases ($AzOH + QOH$), must be substantially equal to $AzOH$; and that the sum of the two ions ($Q + Az$) must be substantially identical with Q . It therefore follows:

$$\frac{OH \times Q}{AzOH} = K_i \quad (9)$$

where K_i expresses the equilibrium relations of the two tautomeric bases and their ions, and is substantially the equation derived by Stieglitz.¹

Combining Equation 9 with that of the ion product of water $H \times OH = K_w$, we get:

$$\frac{H \times AzOH}{Q} = \frac{K_w}{K_i} = K_{(hydrolysis)} \quad (10)$$

which is in reality the familiar equation of Walker² ($\frac{\text{acid} \times \text{base}}{\text{salt}} = k$).

Having determined the hydrolysis constant according to Equation 10, the ionization constant K_i of methyl orange as a base can readily be obtained. The procedure, then, is to determine by radiometric measurements, the concentrations of Q , H and $AzOH$ in solutions of methyl orange containing varying amounts of these constituents. A method was developed whereby the concentration of the quinoid ions Q in Equation 10 could be determined from the light transmitted by the indicator solutions. The percentage transmissions for these solutions were given by the radiomicrometer deflections. The method will be made clear by the following theoretical considerations applied to methyl orange.

If we consider light to pass through an absorbing solution of depth l , the solvent itself having no absorption, the rate of change of intensity dI is given by

$$dI = -kI dl \quad (11)$$

¹ THIS JOURNAL, 25, 1112 (1903).

² Z. physik. Chem., 4, 324 (1889).

The constant k depends only on the wave length of light and the nature of the absorbing medium. If I_0 denotes the intensity of the incident light, then, when $l = 0$, $I_0 = I = \text{constant}$. Integrating, the intensity of the transmitted light I given by an absorbing solution of depth l and concentration c is—

$$I = I_0 e^{-klc}. \quad (12)$$

If the solution has a second absorbing component, the light transmitted by it will be:

$$I_1 = I_0 e^{-k'l'c'}. \quad (13)$$

Since the total transmission is the product of the separate transmissions, we have for the actual percentage transmission of a solution containing two absorbing components such as methyl orange:

$$I/I_0 = e^{-klc - k'l'c'}; \text{ or } \ln(I/I_0) = -klc - k'l'c'. \quad (14)$$

Since the depth of solution was maintained constant (20 mm.), the above equation becomes—

$$\ln(I/I_0) = -Kc - K'c'. \quad (15)$$

Applying this equation to methyl orange, let c represent the concentration of the quinoid salt or Q in Equation 10, and c' that of the azo-base. If T is the total quantity of methyl orange in solution, then $c' = (T - c)$; or since a dibasic acid was used, *viz.*, sulfuric acid, $c' = (T - 2c)$. When a pure solution of methyl orange is slightly acidified with sulfuric acid, and not all of the azo-base converted into the quinoid salt, both c and c' are present. The light transmitted by such a solution will be:

$$\ln(I/I_0) = -Kc - K'(T - 2c). \quad (16)$$

In a pure aqueous solution of methyl orange, or one containing an excess of alkali, $c = 0$, therefore, Equation 15 reduces to:

$$\ln(I/I_0)' = -K'c' = -K'T. \quad (17)$$

If to a solution of methyl orange sufficient sulfuric acid is added to convert all of the azo-base into the quinoid salt and completely suppress hydrolysis, $c' = 0$, and Equation 15 becomes:

$$\ln(I/I_0)'' = -Kc = -KT/2. \quad (18)$$

From Equations 16, 17 and 18, K and K' can be eliminated, and solving for c we obtain:

$$c = \frac{T[\ln(I/I_0) - \ln(I/I_0)']}{2[\ln(I/I_0)'' - \ln(I/I_0)']} \quad (19)$$

In the above equation $(I/I_0)'$ is the percentage transmission for the solution of pure methyl orange for some given wave length of light; $(I/I_0)''$ the percentage transmission of the solution containing an excess of acid for the same wave length, and (I/I_0) the percentage transmission for the same wave length of the solution whose quinoid salt concentration c , is to be determined.

Returning now to the fundamental hydrolysis equation for methyl orange previously derived:

$$\frac{H \times AzOH}{Q^+} = \frac{K_w}{K_i},$$

we can readily insert the proper values knowing the total concentration of methyl orange T , and having determined by radiometric means the quinoid salt concentration c . Q is equal to $2c$. $AzOH = c' = T - 2c$.

H is given by $2(T' - c)$, where T' represents the total quantity of acid added. It is assumed that the dissociation of these extremely dilute solutions is practically complete. The sulfonic acid group can have but little effect upon the hydrogen ion concentration, since benzenesulfonic acid¹ is as strong as sulfuric acid, being dissociated at 25° to the extent of 90% for a dilution $v = 32$. As Stieglitz² has pointed out the whole behavior of methyl orange is that of a very weak base, and the elimination of the sodium sulfonate group from it leaves dimethylaniline azobenzene, which shows all the characteristics of methyl orange as an indicator.

It will be noticed from Equation 10 that it is necessary to know the ionization constant for water, before the constant for the indicator can be calculated from its hydrolysis constant. The generally accepted value of K_w at 25° is 1.2×10^{-14} . It was desired to know the value of the constant at 20° , since, unless otherwise stated, it was at this temperature that all measurements were made. Owing to the large value of the heat of ionization of water, the value of its ionization constant is much less at 20° than at 25° . Just what this change is may be calculated from the well known Van't Hoff formula:

$$\ln \frac{K_1}{K_2} = \frac{q}{R} \left(\frac{T_2 - T_1}{T_2 \times T_1} \right) \quad (20)$$

where K_1 and K_2 represent the ionization constants for water at temperatures T_1 and T_2 . R is the gas constant which equals 1.986 calories per degree, and q is the heat of ionization of water or 13,700 calories. Inserting these values in Equation 20, $K_w = 0.81 \times 10^{-14}$ at 20° . This value was used for the calculation of the ionization constants of both methyl orange and phenolphthalein.

Experimental Work on Methyl Orange.—Before discussing the tables showing the results of the calculations based on the above deductions, it will perhaps be of interest to consider a few of the more important results of the preliminary work on methyl orange. Two mother solutions of known concentrations were prepared, the one being methyl orange and the other sulfuric acid. All solutions were made up at 20° , and carefully

¹ Publication of the Carnegie Institution of Washington, No. 170, 128 (1912).

² THIS JOURNAL, 25, 1117 (1903).

purified substances dissolved in conductivity water, were employed in all cases. A number of test solutions were prepared from the mother solutions, all of which contain equal amounts of methyl orange but different amounts of sulfuric acid. The volume of each solution was 100 cc. The solutions thus presented a series of color shades, ranging from yellow to deep red. The percentage transmissions I/I_0 , were taken with a 20 mm. depth of each solution for the same four or five wave lengths of light. The region of the spectrum to be studied is given by the ascending arm of the transmission curve for methyl orange. This region for the above named indicator is between $\lambda = 0.56\mu$ and $\lambda = 0.59\mu$. The radiomicrometer deflections in this region are necessarily small, and certain variations which appear in the data can be explained in a large measure as due to the vibrations of the building, which often prevented accurate readings.

Special attention is called to a solution of methyl orange containing an excess of alkali, and another solution containing an excess of acid. Equation 19 shows that the calculation of c depends not only on the percentage transmission of the solution in question, but also on the percentage transmission for a solution in which all of the methyl orange exists as the azo-base, and one in which all of the indicator has been converted into the quinoid salt. It is thus necessary to know if any alkali must be added to convert all of the methyl orange into the azo-base and to prevent hydrolysis; and also how much acid is required to form the quinoid salt and to completely suppress hydrolysis. Furthermore, the stability of these solutions must be considered.

Table II shows that in a pure aqueous solution of methyl orange, there is no appreciable hydrolysis, and that practically all of the indicator exists as the azo-base. It is, therefore, not necessary to add alkali in determining the value of $(I/I_0)'$ in Equation 19. The volume of all solutions used in Table II was 100 cc. and each solution contained the same amount of methyl orange.

- I Methyl orange in pure water.
- II Methyl orange plus 1 cc. *N* sodium hydroxide.
- III Methyl orange plus 2.5 cc. *N* sodium hydroxide.

TABLE II.
 I/I_0 for depth of solution = 20 mm.

| λ - Å. U. | I. | II. | III. |
|-------------------|------|------|------|
| 5648 | 70.3 | 71.2 | 70.5 |
| 5698 | 79.3 | 78.8 | 79.0 |
| 5748 | 84.6 | 86.0 | 84.8 |
| 5797 | 90.0 | 90.0 | 88.5 |
| 5847 | 91.4 | 92.2 | 90.0 |

Table III gives results for three solutions of methyl orange, each containing an excess of acid and the same amount of indicator diluted to 100 cc.

- I Methyl orange plus 0.2 cc. concentrated sulfuric acid.
 II Methyl orange plus 0.5 cc. concentrated sulfuric acid.
 III Methyl orange plus 1.0 cc. concentrated sulfuric acid.

TABLE III.
 I/I₀ for depth of solution = 20 mm.

| $\lambda = \text{\AA. U.}$ | I. | II. | III. |
|----------------------------|------|------|------|
| 5698 | 15.2 | 15.2 | 16.6 |
| 5723 | 20.2 | 20.1 | 20.1 |
| 5748 | 30.7 | 31.2 | 31.9 |
| 5773 | 39.5 | 39.2 | 38.8 |
| 5797 | 48.7 | 49.2 | 48.1 |
| 5823 | 55.0 | 53.8 | 55.3 |
| 5847 | 61.4 | 62.6 | 63.2 |

It is obvious from Table III, that 0.2 cc. of the acid is sufficient to convert all of the azo-base into the quinoid salt and to suppress hydrolysis completely.

Stable solutions of methyl orange are given only when the concentration is less than 2×10^{-4} gram molecules per liter. Considerable difficulty was encountered during the preliminary work, owing to the fact that the indicator solutions were more concentrated than the above named limit. Such solutions of methyl orange, especially those containing a large excess of acid and also those with enough acid to give an intense red color, gradually become more transparent on standing. The action of light very greatly accelerates this bleaching process. The solutions most susceptible to the action of light and of time are those containing the greatest amounts of acid. It was found that these solutions could be kept in the dark for four or five hours unchanged, and that as soon as they were exposed to the light, bleaching again took place. Experiments were made which showed that light of the shorter wave lengths was more actinic in increasing the transparency of the solutions than light of longer wave lengths. The addition of ten per cent of ethyl alcohol rendered these solutions fairly stable against the action of light and time. After standing for a day or two, solutions containing an excess of acid often showed the presence of fine crystals. Large amounts of these crystals could be obtained by strongly acidifying a saturated solution of methyl orange. It is thought that the formation of these crystals, very probably helianthine itself, causes the instability of the solutions in question. The obvious procedure to follow was to use more dilute solutions, which were found to be quite stable, and even the solution containing the excess of acid would remain practically unchanged when exposed to the action of light for a short time. However, when the concentration of methyl orange approximated 2×10^{-4} gram-molecules per liter, as is the case for the solutions given in Table IV, the solution containing an excess of acid was prepared last and its percentage transmission measured immediately. The remaining solutions were

kept in the dark until used. It is certain that when such precautions are taken, no appreciable change in transparency could occur before the radiometric measurements were completed. Table III, the concentration of the methyl orange being 1.98×10^{-4} gram-molecules-per liter, shows that even the solutions containing an excess of acid can be safely used in this way.

The following shows how accurately small concentrations of hydrogen and hydroxyl ions can be estimated by radiometric measurements. If the percentage transmission for the various solutions be plotted as curves, the abscissas being wave lengths and the ordinates percentage transmissions, it will be noted that with increasing amounts of acid the transmission curve for pure methyl orange is widely displaced towards the red end of the spectrum. The solution curve corresponding to the excess of acid is displaced about 400 Ångstrom units from the curve corresponding to a pure aqueous solution of methyl orange. From the displacements produced by solutions containing known amounts of acid, and the displacement given by a solution containing an unknown amount, the concentration of the unknown amount of acid can be quite accurately and quickly determined. In one case a solution was prepared containing an amount of sulfuric acid unknown to us. The concentration of the acid was determined by the above method, and the value found was 0.00000216 gram per cc. The amount actually present was 0.00000210 gram per cc. Several similar attempts were made and they were quite as successful.

Results with Methyl Orange.—The hydrolysis and ionization constants for methyl orange, recorded in Tables V and VII, are to be regarded as part of the preliminary work. Table IV contains the percentage transmissions for nine solutions of methyl orange prepared in accordance with the scheme given below. The concentration of the mother solutions of methyl orange was 3.973×10^{-4} ; that of the mother solution of sulfuric acid 3.0885×10^{-4} gram-molecules per liter.

SOLUTIONS.

- I 50 cc. methyl orange, diluted to 100 cc.
- II 50 cc. methyl orange, 5 cc. sulfuric acid, diluted to 100 cc.
- III 50 cc. methyl orange, 10 cc. sulfuric acid, diluted to 100 cc.
- IV 50 cc. methyl orange, 15 cc. sulfuric acid, diluted to 100 cc.
- V 50 cc. methyl orange, 20 cc. sulfuric acid, diluted to 100 cc.
- VI 50 cc. methyl orange, 30.9 cc. sulfuric acid, diluted to 100 cc.
- VII 50 cc. methyl orange, 35 cc. sulfuric acid, diluted to 100 cc.
- VIII 50 cc. methyl orange, 1.0 cc. conc. sulfuric acid, diluted to 100 cc.
- IX 50 cc. methyl orange, 2.0 cc. conc. sulfuric acid, diluted to 100 cc.

TABLE IV.

| | | I/I ₀ for depth of solution = 20 mm. | | | | | | | | Average of VIII and IX. |
|----------|------|---|------|------|------|------|------|-------|------|-------------------------------|
| λ= Å. U. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | IX. | |
| 5748 | 84.6 | .. | 71.9 | 65.1 | 57.7 | 49.1 | 46.7 | 9.5 | 8.4 | 8.95 |
| 5798 | 90.0 | 85.6 | 79.3 | 73.3 | 70.0 | 62.2 | 61.0 | 22.1 | 22.1 | 22.1 |
| 5847 | 91.4 | .. | 84.6 | 81.4 | 77.9 | 70.3 | .. | 35.7 | 35.7 | 35.7 |

Attention is called to the blank spaces appearing in some of the tables. For some solutions and certain wave lengths of light no transmission values were obtained. It was known at the time the measurements were made that certain transmission values were erroneous, due either to variations in the current intensity or to vibrational disturbances. The action of light, as has been previously explained, renders these solutions of methyl orange more transparent, and for this reason it was necessary to complete the reading as soon as possible. This excluded the possibility of remeasuring the percentage transmissions made when conditions were unfavorable for accurate readings.

Table V gives the quinoid salt and azo-base concentrations of each of the above solutions, the hydrolysis constant (K_w/K_i), and the ionization constant K_i of methyl orange as a base.

TABLE V.

| Solution. | $\lambda = \text{\AA. U.}$ | Azo-base $c' \times 10^4$. | Quinoid salt. $c \times 10^4$. | $K_w/K_i \times 10^4$. | $K_i \times 10^{11}$. |
|-----------|----------------------------|--------------------------------|------------------------------------|-------------------------|------------------------|
| II..... | 5798 | 1.91 | 0.353 | 6.5 | 1.3 |
| III..... | 5748 | 1.84 | 0.716 | 6.1 | 1.3 |
| | 5797 | 1.80 | 0.897 | 4.4 | 1.8 |
| | 5847 | 1.82 | 0.813 | 5.1 | 1.6 |
| IV..... | 5748 | 1.75 | 1.16 | 5.2 | 1.6 |
| | 5797 | 1.69 | 1.46 | 3.7 | 2.2 |
| | 5847 | 1.74 | 1.23 | 4.8 | 1.7 |
| V..... | 5748 | 1.64 | 1.69 | 4.4 | 1.9 |
| | 5797 | 1.63 | 1.78 | 4.0 | 2.0 |
| | 5847 | 1.65 | 1.68 | 4.4 | 1.8 |
| VI..... | 5748 | 1.50 | 2.41 | 4.5 | 1.8 |
| | 5797 | 1.46 | 2.61 | 3.9 | 2.0 |
| | 5847 | 1.43 | 2.76 | 3.5 | 2.3 |
| VII..... | 5847 | 1.46 | 2.62 | 4.6 | 1.8 |
| | 5797 | 1.46 | 2.65 | 4.5 | 1.8 |

Av., 4.5×10^{-4} Av., 1.8×10^{-11}

The calculations of the hydrolysis and ionization constants are based on logarithmic functions; and where the transmission of the solution is nearly complete, a slight variation from the actual percentage transmission will cause a great change in the calculated hydrolysis and ionization constants. If we consider an experimental case where the amount of absorption to be measured is slight, the above can be made quite clear. Solution II in Table IV for wave length of light $\lambda = 5798 \text{ \AA. U.}$ actually gave a percentage transmission of 85.6. Changing the percentage transmission by small amounts, and calculating the value of the hydrolysis and ionization constants from these values, we obtain:

| I/I_0 . | K_w/K_i . | K_i . | |
|-----------|-----------------------|------------------------|----------------------|
| 85.6 | 6.46×10^{-4} | 1.25×10^{-11} | found experimentally |
| 86.0 | 7.21×10^{-4} | 1.12×10^{-11} | |
| 86.6 | 8.59×10^{-4} | 0.94×10^{-11} | |

It will thus be seen that changing the percentage transmission by about 1% will cause a variation in the ionization constant of about 25%. When conditions are not satisfactory, it is quite possible that the error in some of the percentage transmissions may be greater than one per cent. Considering these facts, the constants show that the efforts which were made to eliminate errors arising from variations of the current intensity and vibrational disturbances, were fairly successful.

The transmission values given in Table VI are for a much more dilute solution of methyl orange. The concentration of the mother solution of methyl orange was 1.9865×10^{-4} gram-molecules per liter; that of the mother solution of sulfuric acid being 3.0885×10^{-4} gram-molecules per liter.

SOLUTIONS.

- I 50 cc. methyl orange, diluted to 100 cc.
- II 50 cc. methyl orange, 10 cc. sulfuric acid, diluted to 100 cc.
- III 50 cc. methyl orange, 15 cc. sulfuric acid, diluted to 100 cc.
- IV 50 cc. methyl orange, 20 cc. sulfuric acid, diluted to 100 cc.
- V 50 cc. methyl orange, 1 cc. conc. sulfuric acid, diluted to 100 cc.
- VI 50 cc. methyl orange, 0.5 cc. conc. sulfuric acid, diluted to 100 cc.
- VII 50 cc. methyl orange, 0.2 cc. conc. sulfuric acid, diluted to 100 cc.
- VIII 50 cc. methyl orange, 0.5 cc. conc. sulfuric acid, diluted to 100 cc.

TABLE VI.

I/I₀ for depth of solution = 20 mm.

| $\lambda - \lambda_0$ U. | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | Average V, VI, VII and VIII. |
|--------------------------|------|------|------|------|------|------|------|-------|------------------------------------|
| 5698 | 87.7 | 75.3 | 67.6 | 66.3 | 16.6 | 15.2 | 15.2 | 17.1 | 16.0 |
| 5723 | 88.9 | 80.7 | 74.2 | 72.3 | 20.1 | 20.1 | 20.2 | .. | 20.1 |
| 5748 | 90.3 | 83.7 | 79.8 | 76.6 | 31.9 | 31.2 | 30.7 | 30.3 | 31.3 |
| 5773 | 91.6 | .. | 81.7 | 81.3 | 38.8 | 39.0 | 39.5 | 41.1 | 39.9 |
| 5797 | 93.5 | 88.9 | 85.1 | 84.4 | 48.1 | 49.2 | 48.7 | 47.5 | 48.4 |
| 5823 | 94.5 | 91.3 | 87.0 | 86.2 | 55.3 | 53.8 | 55.0 | 56.4 | 55.1 |
| 5847 | 95.6 | 91.7 | .. | 88.2 | 63.2 | 62.6 | 61.4 | 61.7 | 62.2 |

The constants given in Table VII are calculated from the values in Table VI.

The ionization constants for methyl orange, recorded in Tables V and VII, do not by any means represent the most accurate values that can be obtained by this radiometric method. It is necessary that the measurements be made in a region of the spectrum where the light energy is not intense, and, consequently, the deflections of the radiomicrometer are small. The largest deflection that could be obtained for wave lengths of light $\lambda = 0.58\mu$ was 60 mm. It is for this reason that vibrations, and variations in the intensity of the Nernst glower, seriously interfere with the accuracy of the percentage transmissions. The temperature which prevailed at the time these measurements were made was not accurately known. However,

it is certain that it was between 20° and 23°. The constants were calculated for 20°; therefore, there is good reason to suppose that the real constants are somewhat higher (See Table IX).

TABLE VII.

| Solution. | $\lambda = \text{\AA. U.}$ | Azo-base $c' \times 10^4$ | Quinoid salt $c \times 10^4$ | $K_w/K_i \times 10^4$ | $K_i \times 10^4$ |
|-----------|----------------------------|------------------------------|---------------------------------|-----------------------|-------------------|
| IV..... | 5698 | 8.30 | 8.14 | 5.5 | .5 |
| | 5723 | 8.55 | 6.88 | 6.8 | .2 |
| | 5748 | 8.41 | 7.62 | 6.0 | .4 |
| | 5773 | 8.49 | 7.18 | 6.4 | .3 |
| | 5797 | 8.42 | 7.56 | 6.0 | .4 |
| | 5823 | 8.22 | 8.56 | 5.1 | .6 |
| | 5847 | 8.06 | 9.36 | 4.5 | .8 |
| III..... | 5698 | 8.42 | 7.58 | 4.3 | .9 |
| | 5723 | 8.72 | 6.03 | 5.8 | .4 |
| | 5748 | 8.78 | 5.76 | 6.2 | .3 |
| | 5773 | 8.55 | 6.88 | 4.9 | .7 |
| | 5797 | 8.54 | 6.95 | 4.8 | .7 |
| | 5823 | 8.40 | 7.63 | 4.3 | .9 |
| II..... | 5698 | 9.04 | 4.47 | 5.3 | .5 |
| | 5723 | 9.28 | 3.24 | 7.9 | .0 |
| | 5748 | 9.22 | 3.53 | 7.1 | .1 |
| | 5797 | 9.20 | 3.62 | 6.9 | .2 |
| | 5823 | 9.28 | 3.22 | 8.0 | .0 |
| | 5847 | 8.96 | 4.84 | 4.8 | .7 |

Av., 5.8×10^{-4} Av., 1.5×10^{-11}

The transmission values given in Table VIII, were obtained when the temperature at the time of measurement was known to be 20°. The measurements were made at night when the building was fairly free from vibrations. Under these conditions, the scale could be read accurately to 0.25 mm. Except for Solutions II and VI, the current intensity remained very constant. A different mother solution of methyl orange was used, its concentration being 3.054×10^{-4} gram-molecules per liter. The concentration of the mother solution of sulfuric acid was 3.089×10^{-4} gram molecules per liter.

SOLUTIONS.

- I 50 cc. methyl orange, diluted to 100 cc.
- II 50 cc. methyl orange, 10 cc. sulfuric acid, diluted to 100 cc.
- III 50 cc. methyl orange, 15 cc. sulfuric acid, diluted to 100 cc.
- IV 50 cc. methyl orange, 20 cc. sulfuric acid, diluted to 100 cc.
- V 50 cc. methyl orange, 25 cc. sulfuric acid, diluted to 100 cc.
- VI 50 cc. methyl orange, 40 cc. sulfuric acid, diluted to 100 cc.
- VII 50 cc. methyl orange, 0.7 cc. conc. sulfuric acid, diluted to 100 cc.
- VIII 50 cc. methyl orange, 0.8 cc. conc. sulfuric acid, diluted to 100 cc.

TABLE VIII.
I/I₀ for depth of solution = 20 mm. Temperature = 20°.

| $\lambda = \text{\AA. U.}$ | I. | II. | III. | IV. | V. | VI. | VII. | VIII. | Average VII and VIII. |
|----------------------------|------|------|------|------|------|------|------|-------|--------------------------|
| 5723 | 88.2 | 71.8 | 63.7 | 58.0 | 51.6 | .. | 11.8 | 11.6 | 11.7 |
| 5748 | 90.0 | 77.6 | 68.6 | 64.0 | 59.8 | .. | 17.1 | 17.6 | 17.4 |
| 5773 | 91.6 | .. | 75.2 | 71.0 | 67.4 | .. | 24.8 | 24.9 | 24.9 |
| 5797 | 93.4 | .. | 78.7 | 76.2 | 72.6 | 63.8 | 32.5 | 33.2 | 32.4 |
| 5848 | 95.4 | 89.6 | 86.6 | 84.5 | .. | 75.2 | 49.0 | 49.8 | 49.4 |
| 5898 | 97.2 | .. | 91.4 | 89.8 | 88.7 | .. | 63.5 | 63.5 | 63.5 |

The values calculated from Table VIII are recorded in Table IX.

TABLE IX.

| Solution. | $\lambda = \text{\AA. U.}$ | Azo-base $c' \times 10^4$. | Quinoid salt. $c \times 10^4$. | K_w/K_i | ϵ . | $K_i \times 10^{11}$. |
|-----------|----------------------------|--------------------------------|------------------------------------|-------------|--------------|----------------------------|
| VI..... | 5797 | 0.975 | 2.76 | 3. | | 2.4 |
| | 5848 | 0.975 | 2.76 | 3. | | 2.4 |
| V..... | 5723 | 1.193 | 1.67 | 4. | | 1.9 |
| | 5748 | 1.147 | 1.99 | 3. | | 2.3 |
| | 5773 | 1.167 | 1.80 | 3. | | 2.1 |
| | 5797 | 1.203 | 1.62 | 4. | | 1.8 |
| | 5898 | 1.197 | 1.65 | 4. | | 1.8 |
| IV..... | 5723 | 1.211 | 1.58 | 3. | | 2.3 |
| | 5748 | 1.211 | 1.58 | 3. | | 2.3 |
| | 5773 | 1.227 | 1.50 | 3. | | 2.1 |
| | 5798 | 1.235 | 1.46 | 4. | | 2.0 |
| | 5848 | 1.315 | 1.36 | 4. | | 1.8 |
| | 5898 | 1.245 | 1.42 | 4. | | 1.9 |
| III..... | 5723 | 1.281 | 1.23 | 3. | | 2.3 |
| | 5748 | 1.277 | 1.25 | 3. | | 2.3 |
| | 5773 | 1.295 | 1.16 | 3. | | 2.1 |
| | 5798 | 1.269 | 1.24 | 3. | | 2.3 |
| | 5848 | 1.309 | 1.09 | 4. | | 1.9 |
| | 5898 | 1.301 | 1.13 | 4. | | 2.0 |
| II..... | 5723 | 1.372 | 0.773 | 4. | | 2.0 |
| | 5748 | 1.390 | 0.687 | 4. | | 1.7 |
| | 5848 | 1.383 | 0.718 | 4. | | 1.8 |
| | | Av., 4 | | (10^{-4}) | | Av., 2.1 $\times 10^{-11}$ |

The greatest variation from the mean is less than 20%. It has already been shown in one experimental case, that an error of 1 per cent. in the percentage transmission would cause a variation of 25 per cent. in the ionization constant. The determination of the percentage transmissions from which the constants recorded in Table IX are calculated was made under the most favorable conditions. These constants, therefore, more likely represent the true constants of the indicator.

Phenolphthalein.—Regarding phenolphthalein as a monobasic acid, we have from Equation 2:

$$\frac{Q \times H}{LH} = K_i.$$

Dividing this by the ion product of water, it follows that:

$$\frac{LH \times \overline{OH}}{Q^+} = \frac{K_w}{K_i} \quad (21)$$

Phenolphthalein has but one component of absorption, and the application of Beer's Law is much simpler than for methyl orange where there are two components of absorption. A solution of phenolphthalein in pure water is perfectly transparent. The addition of an excess of sodium hydroxide converts all the colorless lactoid molecules into the red quinoid salt, the concentration of which we will represent by c' . Let c be the concentration of the quinoid salt in the phenolphthalein solutions containing ammonium hydroxide and ammonium chloride. Since the depth of solution was maintained constant, we have the two fundamental equations given below:

$$\ln (I/I_0) = -Kc \quad (22)$$

$$\ln (I/I_0)' = -Kc' \quad (23)$$

The constant K is the same in both cases. Dividing 22 by 23 we obtain:

$$\frac{\ln (I/I_0)}{\ln (I/I_0)'} = c/c' \text{ or } c = \frac{c' \times \ln (I/I_0)}{\ln (I/I_0)'} \quad (24)$$

Where $(I/I_0)'$ is the percentage transmission of a solution of phenolphthalein containing an excess of alkali, for some given wave length of light; (I/I_0) that for the solution in which the concentration of the quinoid salt c , is to be determined for the same wave length of light. Knowing then, the amount of phenolphthalein converted into the quinoid salt, LH in Equation 21 is given by $T - c$, where T represents the total amount of phenolphthalein. The hydroxyl ion concentration was varied by the addition of ammonium chloride to ammonium hydroxide.

The value of \overline{OH} to be substituted in the hydrolysis equation for phenolphthalein was obtained from the following equation:

$$\frac{NH_4^+ \times \overline{OH}}{(NH_4OH + NH_3)} = K_b.$$

If ammonium chloride and ammonium hydroxide are present in the same solution, the concentration of the NH_4 ions is furnished almost entirely by the ammonium chloride. Let S equal the concentration of the salt and B the concentration of the base. We then have for dilute solutions:

$$\frac{S \times \overline{OH}}{B} = K_b \quad (25)$$

or

$$\overline{OH} = \frac{K_b \times B}{S} \quad (26)$$

The ionization constant for ammonium hydroxide¹ at 25° is given as 18×10^{-6} . All of the work on phenolphthalein was done at 20°, and reducing the above value to 20°, we obtain from Equation 20, q being equal to 1400 calories, $K_b = 17.4 \times 10^{-6}$.

A pure sample of phenolphthalein was recrystallized from absolute methyl alcohol. A weighed amount of purified phenolphthalein was dissolved in 50 cc. of absolute ethyl alcohol. By means of a small pipet, carefully calibrated, a small volume of this alcoholic solution, say 1.25 cc., could be quite accurately measured. This volume was diluted with conductivity water to 2000 cc. Experiments were made which showed that the effect of this small trace of alcohol was negligible. (See McCoy.²) The ammonia employed for the solution of ammonium hydroxide, was distilled from barium hydroxide to eliminate carbon dioxide. All solutions were prepared with conductivity water at 20°. Special care was taken to prevent carbon dioxide from coming in contact with any of the solutions.

It is well known that an excess of alkali causes a rather rapid fading of solutions of phenolphthalein. Experiments were made which showed that a very slight error would be introduced, if the solutions of phenolphthalein containing an excess of alkali were used directly after being prepared. Filling the cells with the solution, and taking radiometric measurements for five wave lengths of light, required about eight minutes, and during this short space of time, the change in transparency was found to be very slight.

A few of the experiments made with solutions of phenolphthalein containing an excess of alkali are recorded in Table X. All solutions were diluted to 100 cc., and each contained equal amounts of phenolphthalein. A normal solution of sodium hydroxide was used for these experiments. The percentage transmissions given by Solutions I and II are for 0.8 cc. and 1 cc., respectively, of the alkali. The interval which elapsed between the time the solutions were prepared and the last measurement made, was between seven and eight minutes. Measurements were again made with Solution II, fifteen minutes later. The results are recorded under III. By comparing the transmission values, the effect of the bleaching for an interval of fifteen minutes can be noted. Solution IV contained 0.5 cc. alkali, and was kept in the dark nearly a half-hour before being used. Solution V containing 1 cc. of alkali, was used about four hours after being prepared.

Similar experiments were made with solutions of phenolphthalein, partially converted into the quinoid salt, and it was found that such solutions are fairly stable. Very little change in transparency could be detected during the first four or five hours after the solutions were prepared.

¹ Publication of the Carnegie Institution of Washington, No. 63, 298 (1907).

² *Loc. cit.*

TABLE X.
I/I₀ for depth of solution = 20 mm.

| $\lambda = \text{\AA. U.}$ | I. | II. | III. | IV. | V. |
|----------------------------|------|------|------|------|------|
| 5773 | 10.5 | 10.1 | 12.1 | 10.1 | 24.9 |
| 5798 | 15.2 | 15.4 | 16.5 | 15.2 | 31.0 |
| 5823 | 20.8 | 20.2 | 22.6 | 21.4 | 37.8 |
| 5848 | 28.7 | 27.4 | 30.3 | 28.4 | 45.6 |
| 5947 | 59.4 | 57.7 | 61.2 | 60.3 | 71.1 |

Results with Phenolphthalein.—The six solutions recorded below were prepared from the following mother solutions: The concentration of the phenolphthalein was 6.697×10^{-5} gram-molecules per liter; that of the ammonium hydroxide 0.1448 gram-molecules per liter, and that of the ammonium chloride 0.1 gram-molecules per liter.

SOLUTIONS.

- I 75 cc. phenolphthalein, diluted to 100 cc.
 II 75 cc. phenolphthalein, 2 cc. NH_4OH , 1 cc. NH_4Cl , diluted to 100 cc.
 III 75 cc. phenolphthalein, 2 cc. NH_4OH , 2 cc. NH_4Cl , diluted to 100 cc.
 IV 75 cc. phenolphthalein, 2 cc. NH_4OH , 5 cc. NH_4Cl , diluted to 100 cc.
 V 75 cc. phenolphthalein, 2 cc. NH_4OH , 10 cc. NH_4Cl , diluted to 100 cc.
 VI 75 cc. phenolphthalein, 1 cc. N NaOH , diluted to 100 cc.

TABLE XI.
I/I₀ for depth of solution = 20 mm. Temperature = 20°.

| $\lambda = \text{\AA. U.}$ | I. | II. | III. | IV. | V. | VI. |
|----------------------------|-------|------|------|------|------|------|
| 5773 | 100.0 | 30.8 | 46.3 | 70.7 | .. | 10.1 |
| 5798 | 100.0 | 37.8 | 53.4 | 76.3 | 86.7 | 14.3 |
| 5823 | 100.0 | 45.3 | 58.9 | 78.5 | 89.3 | 20.2 |
| 5848 | 100.0 | 51.7 | 66.2 | 83.0 | 91.3 | 27.4 |
| 5948 | 100.0 | .. | 83.7 | .. | .. | 57.7 |

TABLE XII.

| Solutions. | $\lambda = \text{\AA. U.}$ | Lactoid form $c \times 10^4$. | Quinoid salt $c \times 10^4$. | $\text{OH} \times 10^4$. | K_w/K_i $\times 10^4$. | $K_i \times 10^{10}$. | Average $K_i \times 10^{10}$. |
|------------|----------------------------|-----------------------------------|-----------------------------------|---------------------------|------------------------------|------------------------|-----------------------------------|
| II..... | 5773 | 2.44 | 2.58 | 5.039 | 4.77 | 1.70 | .. |
| | 5798 | 2.51 | 2.51 | 5.039 | 5.05 | 1.60 | 1.63 |
| | 5823 | 2.54 | 2.48 | 5.039 | 5.17 | 1.57 | .. |
| | 5848 | 2.46 | 2.56 | 5.039 | 4.85 | 1.67 | .. |
| III..... | 5773 | 3.33 | 1.69 | 2.519 | 4.96 | 1.64 | .. |
| | 5798 | 3.40 | 1.62 | 2.519 | 5.27 | 1.54 | .. |
| | 5823 | 3.35 | 1.67 | 2.519 | 5.06 | 1.60 | 1.56 |
| | 5848 | 3.42 | 1.60 | 2.519 | 5.38 | 1.51 | .. |
| IV..... | 5948 | 3.40 | 1.62 | 2.519 | 5.28 | 1.53 | .. |
| | 5773 | 4.26 | 0.757 | 1.007 | 5.68 | 1.43 | .. |
| | 5798 | 4.32 | 0.696 | 1.007 | 6.27 | 1.29 | 1.38 |
| | 5823 | 4.26 | 0.761 | 1.007 | 5.63 | 1.44 | .. |
| V..... | 5848 | 4.30 | 0.720 | 1.007 | 6.02 | 1.35 | .. |
| | 5798 | 4.65 | 0.369 | 0.503 | 6.37 | 1.27 | .. |
| | 5823 | 4.67 | 0.356 | 0.503 | 6.63 | 1.22 | 1.23 |
| | 5848 | 4.67 | 0.352 | 0.503 | 6.68 | 1.21 | .. |

The percentage transmissions for these solutions are given in Table XI. The concentrations of the two tautomeric forms, and the hydrolysis and ionization constants calculated from Table XI, are recorded in Table XII.

The series of solutions, the results of which are recorded in Table XIII, were prepared from another solution of phenolphthalein. Its concentration was 4.603×10^{-5} gram-molecules per liter. The concentrations of the ammonium hydroxide and ammonium chloride solutions were the same as for the previous series. It will be noticed that 1 cc. of a solution of ammonium hydroxide was used instead of 2 cc. as in the former case.

SOLUTIONS.

- I 75 cc. phenolphthalein, 1 cc. NH_4OH , 0.5 cc. NH_4Cl , diluted to 100 cc.
 II 75 cc. phenolphthalein, 1 cc. NH_4OH , 1 cc. NH_4Cl , diluted to 100 cc.
 III 75 cc. phenolphthalein, 1 cc. NH_4OH , 2 cc. NH_4Cl , diluted to 100 cc.
 IV 75 cc. phenolphthalein, 1 cc. NH_4OH , 2.5 cc. NH_4Cl , diluted to 100 cc.
 V 75 cc. phenolphthalein, 0.8 cc. $N \text{ NaOH}$, diluted to 100 cc.

TABLE XIII.

I/I₀ for depth of solution = 20 mm. Temperature 20°.

| λ -Å. U. | I. | II. | III. | IV. | V. |
|------------------|------|------|------|------|------|
| 5773 | 48.2 | 62.2 | 73.0 | 81.3 | 15.7 |
| 5798 | 54.2 | 66.3 | 78.7 | 83.0 | 22.7 |
| 5823 | 59.6 | 70.7 | 83.9 | 86.0 | 30.5 |
| 5848 | 66.4 | 74.6 | 85.1 | 89.0 | 37.9 |
| 5948 | 84.8 | 87.7 | .. | 94.8 | 62.2 |

TABLE XIV.

| Solution. | λ -Å. U. | Lactoid form $c \times 10^4$. | Quinoid salt $c \times 10^4$. | $\text{OH} \times 10^4$. | K_w/K_i $\times 10^4$. | $K_i \times 10^{10}$. | Average $K_i \times 10^{10}$. |
|-----------|------------------|-----------------------------------|-----------------------------------|---------------------------|------------------------------|------------------------|-----------------------------------|
| I..... | 5773 | 2.09 | 1.36 | 5.039 | 7.79 | 1.04 | .. |
| | 5798 | 2.03 | 1.42 | 5.039 | 7.24 | 1.12 | 1.14 |
| | 5823 | 1.95 | 1.50 | 5.089 | 6.56 | 1.23 | .. |
| | 5848 | 1.99 | 1.46 | 5.039 | 6.92 | 1.17 | .. |
| II..... | 5773 | 2.56 | 0.884 | 2.519 | 7.31 | 1.11 | .. |
| | 5798 | 2.49 | 0.953 | 2.519 | 6.61 | 1.23 | .. |
| | 5823 | 2.44 | 1.006 | 2.519 | 6.13 | 1.32 | 1.25 |
| | 5848 | 2.41 | 1.040 | 2.519 | 5.83 | 1.39 | .. |
| | 5948 | 2.49 | 0.951 | 2.519 | 6.61 | 1.23 | .. |
| III..... | 5773 | 2.86 | 0.587 | 1.259 | 6.15 | 1.32 | .. |
| | 5798 | 2.89 | 0.557 | 1.259 | 6.53 | 1.24 | 1.21 |
| | 5823 | 2.94 | 0.508 | 1.259 | 7.96 | 1.02 | .. |
| | 5848 | 2.87 | 0.573 | 1.259 | 6.37 | 1.27 | .. |
| IV..... | 5773 | 3.05 | 0.386 | 1.007 | 8.03 | 1.01 | .. |
| | 5798 | 3.01 | 0.433 | 1.007 | 7.01 | 1.15 | .. |
| | 5823 | 3.01 | 0.436 | 1.007 | 7.01 | 1.15 | 1.06 |
| | 5848 | 3.03 | 0.413 | 1.007 | 7.42 | 1.09 | .. |
| | 5948 | 3.06 | 0.385 | 1.007 | 8.04 | 1.01 | .. |

The concentrations of the mother solutions used in the preparation of the solutions for the following series of measurements, were the same as those employed for Table XI. The results are recorded in Tables XV and XVI.

SOLUTIONS.

- I 75 cc. phenolphthalein, 0.5 cc. NH_4OH , 0.5 cc. NH_4Cl , diluted to 100 cc.
 II 75 cc. phenolphthalein, 0.5 cc. NH_4OH , 1 cc. NH_4Cl , diluted to 100 cc.
 III 75 cc. phenolphthalein, 0.5 cc. NH_4OH , 2 cc. NH_4Cl , diluted to 100 cc.
 IV 75 cc. phenolphthalein, 0.8 cc. N NaOH, diluted to 100 cc.

TABLE XV.

I/I_0 for depth of solution = 20 mm. Temperature = 20° .

| $\lambda = \text{\AA. U.}$ | I. | II. | III. | IV. |
|----------------------------|------|------|------|------|
| 5773 | 63.2 | 76.2 | 87.3 | 9.9 |
| 5798 | 65.8 | 80.3 | 89.2 | 14.7 |
| 5823 | 72.0 | 82.8 | 91.5 | 20.4 |
| 5848 | 74.3 | .. | .. | 27.4 |
| 5948 | 88.8 | 93.3 | .. | 57.6 |

TABLE XVI.

| Solution. | $\lambda = \text{\AA. U.}$ | Lactoid form $c \times 10^3$ | Quinoid salt $c \times 10^3$ | $\text{OH} \times 10^3$ | K_w/K_i $\times 10^4$ | $K_i \times 10^{10}$ | Average $K_i \times 10^{10}$ |
|-----------|----------------------------|------------------------------------|------------------------------------|-------------------------|----------------------------|----------------------|---------------------------------|
| I..... | 5773 | 4.026 | 0.99 | 2.519 | 10.16 | 0.80 | .. |
| | 5798 | 3.935 | 1.09 | 2.519 | 9.07 | 0.99 | .. |
| | 5823 | 3.985 | 1.04 | 2.519 | 9.65 | 0.83 | 0.89 |
| | 5848 | 3.875 | 1.15 | 2.519 | 8.47 | 0.97 | .. |
| | 5948 | 3.955 | 1.07 | 2.519 | 9.28 | 0.87 | .. |
| II..... | 5773 | 4.43 | 0.59 | 1.26 | 9.46 | 0.86 | .. |
| | 5798 | 4.45 | 0.57 | 1.26 | 9.77 | 0.83 | 0.87 |
| | 5823 | 4.42 | 0.60 | 1.26 | 9.24 | 0.88 | .. |
| | 5948 | 4.39 | 0.62 | 1.26 | 8.82 | 0.92 | .. |
| III..... | 5773 | 4.73 | 0.30 | 0.63 | 10.07 | 0.81 | .. |
| | 5798 | 4.73 | 0.30 | 0.63 | 10.00 | 0.81 | 0.79 |
| | 5823 | 4.74 | 0.28 | 0.63 | 10.65 | 0.75 | .. |

The concentration of phenolphthalein is not a factor in the variations of the constants in the different tables. The following shows that it is possible to determine K_i without knowing the concentration of the indicator.

If we consider Equation 21—

$$\frac{\text{LH} \times \text{OH}}{Q^+} = \frac{K_w}{K_i}$$

and represent the total concentration of phenolphthalein by T , and that of the quinoid salt by Q , we have from Equation 24:

$$\frac{\ln(I/I_0) \times T}{\ln(I/I_0)'} = Q.$$

LH is then equal to $(T - Q)$ or,

$$LH = (T - Q) = T - \frac{\ln(I/I_o) \times T}{\ln(I/I_o)'} \quad (27)$$

Substituting these values in the hydrolysis equation, we have:

$$\frac{\left[T - \frac{\ln(I/I_o) \times T}{\ln(I/I_o)'} \right] \times \bar{OH}}{\frac{\ln(I/I_o) \times T}{\ln(I/I_o)'}} = \frac{K_w}{K_i} \quad (28)$$

Simplifying, T , the concentration of the phenolphthalein disappears, and we have:

$$\frac{\bar{OH}[\ln(I/I_o)' - \ln(I/I_o)]}{\ln(I/I_o)} = \frac{K_w}{K_i} \quad (29)$$

K_i , calculated from Equation 29, gives the same value as when calculated from the equations previously derived.

Since it is not necessary to know the concentration of the indicator to determine its ionization constant, the variation of K_i , shown by the different tables, must be due to other causes. It will be noticed from the separate tables that K_i decreases with the hydroxyl ion concentration. This is in accordance with the results of previous investigators. When the hydroxyl ion concentration, or the ratio of ammonium chloride to ammonium hydroxide remains the same, K_i shows a marked decrease with decreasing amounts of neutral salts. If we consider Solutions III and I in Tables XII and XVI, respectively, it will be seen that decreasing the concentration of the neutral salt four times, changes K_i from 1.6×10^{-10} to 0.9×10^{-10} . This is in accord with the results of Rosenstein,¹ who has made a very careful study of the effect of neutral salts on the ionization constant of phenolphthalein. It will, therefore, be seen that the discrepancies in the value of K_i are due in part at least to the effect of the neutral salt. From this it might be concluded that K_i would be largest for those solutions containing the greatest amount of neutral salt. A study of the separate Tables, Table XII for instance, shows that just the reverse is true. The solution which contains the largest amount of neutral salt always gives the smallest concentration of hydroxyl ions, and the K_i value for such a solution is much lower than for a solution containing less neutral salt but a greater concentration of hydroxyl ions. It is thus evident that K_i varies not only with the concentration of the neutral salt, but also with the concentration of the hydroxyl ions. From the above, it will be seen that if the neutral salt had no effect, the variation of K_i in the separate tables would be much greater than it actually is. It is therefore obvious that the equilibrium equations, based on the assumption that phenolphthalein acts as a monobasic acid, do not hold.

¹ *Loc. cit.*

Wegscheider¹ concludes that these variations may be accounted for by regarding phenolphthalein as a dibasic acid. The results of Rosenstein¹ make it appear very probable that this indicator does act as a dibasic acid. The limitations of his method and the presence of neutral salts made it impossible for him to determine satisfactorily the ionization constant for phenolphthalein and the question must therefore be regarded as still open.

The radiometric method has thus far been applied for determining the hydrolysis and ionization constants of indicators. Knowing these values, it is possible, by radiometric means, to determine from them the hydrolysis constants of many salts. The calculation of the ionization constants of weak acids and bases formed by the hydrolysis of these salts is then a simple matter.

This method has been applied in a preliminary way to aluminum sulfate, using methyl orange as the indicator. It is assumed that the secondary and tertiary hydrolysis of this salt can be neglected, and, on this assumption, the ionization constant of the base formed by the primary hydrolysis has been calculated.

The calculations of the constants are based on two fundamental equilibrium equations, the symbols representing gram-ions per liter. Expressing the equilibrium relation for the primary hydrolysis of aluminum sulfate, we have:

$$\frac{\overset{++}{\text{AlOH}} \times \overset{+}{\text{H}}}{\overset{+++}{\text{Al}}} = \frac{K_w}{K_b} \quad (30)$$

In the hydrolysis equation for methyl orange,—

$$\frac{\overset{+}{\text{AzOH}} \times \overset{+}{\text{H}}}{\overset{+}{\text{Q}}} = \frac{K_w}{K_i}$$

K_i has been determined and K_w is known. The concentration of the quinoid ions $\overset{+}{\text{Q}}$ is given by:

$$\overset{+}{\text{Q}} = \frac{\overset{+}{T} [\ln (\overset{+}{I}/\overset{+}{I}_0) - \ln (\overset{+}{I}/\overset{+}{I}_0)']}{\ln (\overset{+}{I}/\overset{+}{I}_0)' - \ln (\overset{+}{I}/\overset{+}{I}_0)'} \quad (31)$$

as explained in Equation 19. If the total amount of indicator is $\overset{+}{T}$, $\overset{+}{\text{AzOH}} = \overset{+}{T} - \overset{+}{\text{Q}}$. We then have all the data necessary for the calculation of the hydrogen ion concentration in Equation 30. The concentration of the ion $\overset{++}{\text{AlOH}}$ in the same equation is given by $\overset{+}{\text{H}} + \overset{+}{\text{Q}}$, both of which have been determined. If $\overset{+++}{T'}$ represents the total salt added and α its dissociation, $\overset{+++}{\text{Al}}$ is $(\overset{+++}{T'} - \overset{+++}{\text{AlOH}}) \alpha$.

¹ *Loc. cit.*

The following solutions were prepared from mother solutions of methyl orange and aluminium sulfate, the concentrations being 1.9865×10^{-4} and 0.391 gram-molecules per liter, respectively.

SOLUTIONS.

- I 50 cc. methyl orange, diluted to 100 cc.
- II 50 cc. methyl orange, 5 cc. $\text{Al}_2(\text{SO}_4)_3$, diluted to 100 cc.
- III 50 cc. methyl orange, 7 cc. $\text{Al}_2(\text{SO}_4)_3$, diluted to 100 cc.
- IV 50 cc. methyl orange, 10 cc. $\text{Al}_2(\text{SO}_4)_3$, diluted to 100 cc.
- V 50 cc. methyl orange, 0.5 cc. conc. H_2SO_4 , diluted to 100 cc.

The percentage transmissions given by these solutions are recorded in Table XVII.

TABLE XVII.

| $\lambda = \text{\AA. U.}$ | I/I ₀ for depth of solution = 20 mm. | | | | |
|----------------------------|---|------|------|------|------|
| | I. | II. | III. | IV. | V. |
| 5698 | 87.7 | 47.7 | 44.7 | 39.7 | 16.0 |
| 5723 | 88.9 | 56.7 | 53.1 | .. | 20.1 |
| 5748 | 90.3 | 63.0 | 59.1 | 56.7 | 31.0 |
| 5773 | 91.6 | 70.2 | 66.8 | 63.6 | 39.9 |
| 5797 | 93.3 | 74.7 | 73.6 | 68.6 | 48.4 |
| 5823 | 94.5 | 78.4 | 78.1 | 75.5 | 55.1 |
| 5847 | 95.6 | 81.6 | .. | 78.5 | 62.2 |

The constants calculated from these percentage transmissions are given in Table XVIII. It has been found¹ that the dissociation of the aluminium sulfate in Solutions II, III and IV, is approximately 35, 32 and 30%, respectively.

TABLE XVIII.

| Solution. | $\lambda = \text{\AA. U.}$ | $\frac{+}{Q}$ 10 ⁴ . | Average AzOH 10 ⁴ . | Average $\frac{+}{H}$ 10 ⁴ . | Average $\frac{++}{AlOH}$ 10 ⁴ . | Average $\frac{+++}{Al}$ 10 ⁴ . | Average $K_m K_b$ $\times 10^4$. | Average $K_b \times 10^4$. |
|-----------|----------------------------|------------------------------------|--------------------------------------|---|---|--|---|--------------------------------|
| II..... | 5698 | 3.56 | .. | .. | .. | .. | .. | .. |
| | 5723 | 3.01 | .. | .. | .. | .. | .. | .. |
| | 5748 | 3.35 | .. | .. | .. | .. | .. | .. |
| | 5773 | 3.20 | 6.56 | 1.97 | 2.307 | 6.76 | 6.75 | 1.2 |
| | 5797 | 3.37 | .. | .. | .. | .. | .. | .. |
| | 5823 | 3.44 | .. | .. | .. | .. | .. | .. |
| | 5847 | 3.65 | .. | .. | .. | .. | .. | .. |
| III..... | 5698 | 3.94 | .. | .. | .. | .. | .. | .. |
| | 5723 | 3.44 | .. | .. | .. | .. | .. | .. |
| | 5748 | 3.94 | 6.24 | 2.24 | 2.609 | 8.66 | 6.75 | 1.2 |
| | 5773 | 3.79 | .. | .. | .. | .. | .. | .. |
| | 5797 | 3.50 | .. | .. | .. | .. | .. | .. |
| | 5823 | 3.51 | .. | .. | .. | .. | .. | .. |
| IV..... | 5698 | 4.62 | .. | .. | .. | .. | .. | .. |
| | 5748 | 4.33 | .. | .. | .. | .. | .. | .. |
| | 5773 | 4.36 | 5.49 | 3.12 | 3.564 | 11.62 | 9.70 | 0.84 |
| | 5797 | 4.66 | .. | .. | .. | .. | .. | .. |
| | 5823 | 4.16 | .. | .. | .. | .. | .. | .. |
| | 5847 | 4.54 | .. | .. | .. | .. | .. | .. |

¹ Publication of the Carnegie Institution of Washington, No. 170, 60 (1912).

Summary.

A satisfactory radiomicrometer, having a half-period of 10 seconds and a sensibility of 5 per square millimeter of exposed vane (candle and scale being at a meter's distance) was constructed.

Making use of the radiomicrometer and the grating spectroscope, a radiometric method was worked out for the determination of the ionization constants of indicators. This method is freer from objections and limitations than any method previously used. It serves as well for a two-colored indicator as for a one-colored indicator.

Very small concentrations of colored components were determined, and it has been shown that minute concentrations of hydrogen and hydroxyl ions can be quickly and accurately estimated by means of radiometric measurements.

Satisfactory constants were obtained for the ionization of methyl orange as a base. The value found is 2.1×10^{-11} .

The ionization and hydrolysis constants for phenolphthalein considered as a monobasic acid are far from being satisfactory.

From the known ionization constant of methyl orange and from radiometric measurements, the ionization constant of a very weak base and the hydrolysis constant of one of its salts have been roughly determined. The method can likewise be applied for the determination of the ionization constants of very weak acids, and the hydrolysis constants of the salts formed by these acids. Work is now in progress in this laboratory on other indicators, from this same standpoint, and the results will soon be published in THIS JOURNAL.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, MD.,
February, 1915.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY:]

THE FRACTIONAL CRYSTALLIZATION OF THE PICRATES OF THE RARE EARTHS OF THE DIDYMIUM GROUP.

By L. M. DENNIS AND F. H. RHODES.

Received February 13, 1913.

The salts of the rare earths with picric acid form well-defined crystals, are much more soluble in hot water than in cold, and crystallize very well from solution. For these reasons, the fractional crystallization of the picrates naturally suggests itself as a method for the separation of the rare earths. Holmberg¹ made a brief examination of this method in the attempt to separate the earths of the terbium group. By the fractional crystallization of the picrates of gadolinium and terbium containing 25 g. of the earths he obtained a rapid concentration of terbium in the first mother liquors and an accumulation of gadolinium in the crystals which

¹ *Z. anorg. Chem.*, 53, 80 (1907).

separated first from the solution. James¹ tried to purify thulium by the fractional crystallization of the picrates, but found that the method is not satisfactory for this purpose.

The work of Holmberg and of James on the fractional crystallization of the picrates was done with small amounts of material and with rare earth mixtures that contained unusual components, and was more or less incidental to other researches. The applicability of the method to the general problem of the separation of the rare earths was investigated systematically for the first time by Dennis and Bennett,² who fractionated a mixture of the picrates of the didymium, erbium, and yttrium groups containing about 1500 g. of the oxides. Fractional crystallization of the neutral solution of the picrates of this material yielded a series of twenty-five final fractions. They determined the atomic weights of the earths in these final fractions and made a comparative study of the absorption spectra of solutions of the chlorides of the earths. They summarized their results as follows:

"... with an original material of an atomic weight of 116, containing earths of the didymium, erbium, and yttrium groups, fractional crystallization of the picrates from aqueous solution yields the following results:

"(1) A concentration of praseodymium and neodymium in the first fractions followed by a rapid decrease of these two elements after the sixth fraction.

"(2) A peculiar increase in the amounts of praseodymium and neodymium in the tenth and nineteenth fractions.

"(3) A sudden concentration of erbium and holmium in the eighth fraction and an entire absence of these two elements in the first six fractions of the series.

"The fractional crystallization of the picrates of the rare earths appears to furnish excellent means of effecting a rapid concentration of praseodymium and neodymium practically free from erbium and holmium, and concentration of erbium and holmium with but relatively small amounts of the members of the didymium group. The peculiar rise in the concentration of praseodymium and neodymium in the tenth and nineteenth fractions is under further investigation."

The work here to be described was undertaken with the object of making careful investigation of the apparently abnormal behavior of the earths of the didymium group upon the fractional crystallization of their picrates.

The original material used in this work consisted of about 25 kg. of the double sodium sulfates of the rare earths obtained as a byproduct in the extraction of thorium from monazite sand and which was kindly presented to us by Dr. H. S. Miner. This material was particularly suited to our purpose because of the relatively large amounts of the earths of the didymium group that it contained. A qualitative analysis of the crude double sulfates revealed the presence of sodium, cerium, and the rare earths, with small amounts of iron, calcium, and silica. No thorium was present. An examination of the absorption spectrum of a concentrated solution of

¹ THIS JOURNAL, 33, 1332 (1911).

² *Ibid.*, 34, 7 (1912).

the chlorides of the rare earths from the double sulfates showed that the material contained large amounts of neodymium and praseodymium. None of the absorption bands of samarium, erbium, or holmium could be detected, even on examining a syrupy solution of the chlorides that was 15 cm. thick.

The difficultly soluble double sulfates of the rare earths were decomposed and converted into the chlorides by the method suggested by Browning and Blumenthal.¹ The material was mixed with about five times its weight of coke dust, and the mixture was placed in large graphite crucibles which were then heated to bright redness for about one hour in crucible assay-furnaces. The reduction of the sulfates took place readily at this temperature, and large volumes of carbon monoxide were evolved. When the reduction was complete, the crucibles were withdrawn and allowed to cool. The mixture of coke dust and sulfides was treated with an excess of commercial concentrated hydrochloric acid. The sulfides of the rare earths dissolved readily with the copious evolution of hydrogen sulfide. As soon as the first vigorous reaction had ceased, the mixture was heated rapidly to boiling to drive off the hydrogen sulfide. The resulting solution of the chlorides of the rare earths was diluted with about six times its own volume of water, allowed to stand until most of the undissolved material had settled out, and then filtered through a Büchner filter. The mass of carbon at the bottom of the cylinder was transferred to the filter, washed thoroughly with hot water, and drained as completely as possible. The finely divided carbon remaining on the filter paper was dried and used for the reduction of further amounts of the crude double sulfates. The oxalates of the rare earths were precipitated by the addition of a solution of oxalic acid to the filtrate after the removal of the carbon. These oxalates were washed, filtered, dried, and ignited to the oxides in bowls of fused quartz heated in a muffle furnace. About 10 kg. of the crude oxides of the rare earths and cerium was obtained. Cerium was next removed by the chlorination method of Mosander. After the material had been subjected to four chlorinations, a solution of the chlorides of the earths from the final filtrate was tested for cerium by making the solution *very faintly* alkaline with ammonium hydroxide and adding hydrogen peroxide. Since no yellow color was produced, cerium was present in no more than minute traces.

From the final solution, after the removal of the cerium, the rare earths were precipitated as the oxalates, which were converted to the oxides by ignition. About 6 kg. of the purified oxides was obtained. The oxides were then dissolved in hydrochloric acid, and the solution was filtered, transferred to large precipitating cylinders, and treated with a slight excess of ammonium hydroxide. The precipitated hydroxides were washed

¹ *Z. anorg. Chem.*, 72, 358 (1911).

by decantation with water until the supernatant liquid was free from chlorides. A qualitative analysis of the washed hydroxides showed the absence of salts of iron, calcium, and ammonium. The average atomic weight of the mixture of rare earths in the purified material was determined by the oxalate method and was found to be 141.48.

There was thus obtained a mixture of the hydroxides of the rare earths of the didymium group, containing small amounts of the earths of the erbium and yttrium groups, but free from cerium, thorium, and the common elements. To convert the hydroxides into the picrates, the suspension of the hydroxides was heated almost to boiling in large pans of enameled ware and a hot solution of picric acid was added in small amounts at a time. In order to insure the formation of a neutral solution of the picrates, the hydroxides were kept always in excess, and the addition of the picric acid was discontinued while a small amount of the hydroxides remained yet undissolved.

The solution of the picrates of the rare earths was diluted with water until it was just saturated at room temperature. The saturated solution was then subjected to fractional crystallization. The first few series of fractionations, involving the concentration of large volumes of solutions, were made in enameled pans holding about forty liters each and heated by means of small gas stoves. As soon as the fractions became sufficiently reduced in size, the crystallization was continued in smaller pans of a capacity of from fifteen to twenty liters. Subsequent fractions of smaller size were concentrated in porcelain evaporators.

The plan of the fractionation is shown in Fig. 1. When an end fraction became too small for further separation it was set aside, and the adjacent fraction became the end fraction in the next series of recrystallizations. Fractions 58, 136, 278, 428, 610, 768, 944, 1008, 1140, 1352, 1504, and 1584 from the soluble end, and fractions 183, 461, 809, 925, 1115, 1323, and 1629 from the insoluble end, were thus removed from further fractionation. When forty-two series of crystallizations had been made, the fractionation was stopped and the fractions of the final series, together with the end fractions set aside during the progress of the fractionation, were examined to determine the nature and the relative amount of the rare earths contained in each.

A considerable difference in the appearance of the crystals and of the mother liquors from the various fractions was observed. The picrates from the less soluble portions of the material crystallized in large plates and columns of an orange-yellow color, while the crystals from the more soluble fractions separated as small bundles of yellow needles. The mother liquors from the less soluble fractions were yellow, while those at the soluble end were of a yellowish brown color. From the first mother liquor set aside from the fractionation at the soluble end, a gelatinous substance

separated on standing. This jelly-like material was analyzed and was found to consist of silica, which had probably been introduced into the original mixture of rare earths from the quartz bowls in which the oxalates had been ignited.

In the examination of the fractions of the final series and of the end fractions set aside during the fractionation, the average atomic weight of

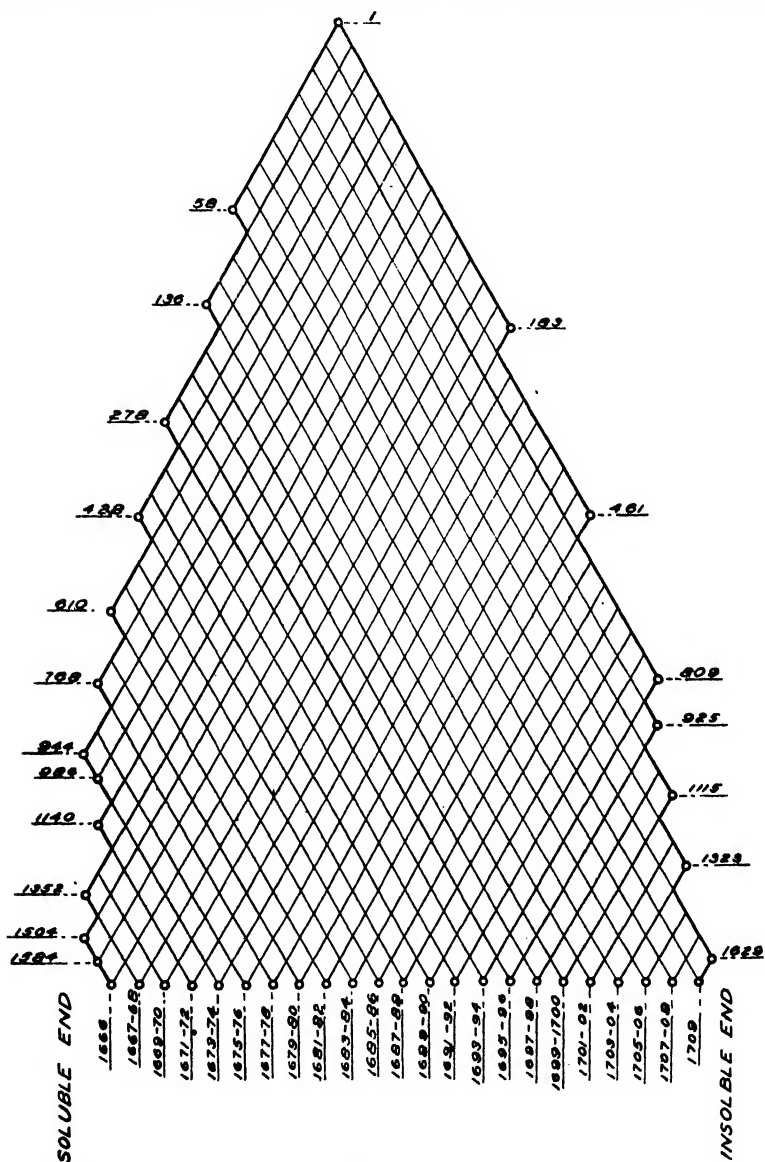


Fig. 1.

the earths in each fraction was determined, and an examination of the absorption spectrum of a solution of the chlorides from each fraction was made.

In the determination of the average atomic weights of the mixtures of rare earths from the various fractions the usual oxalate method was employed. The results of the determination of the average atomic weights of the rare earths from the various fractions were as follows:

| Fraction number soluble end. | Atomic weight. | Color of oxides. | Fraction number soluble end. | Atomic weight. | Color of oxides. |
|---------------------------------|-------------------|---------------------|---------------------------------|-------------------|---------------------|
| 58 | 128.06 | Orange-yellow | 1684-85 | 142.12 | Grey |
| 136 | 118.41 | Orange-yellow | 1686-87 | 141.52 | Grey |
| 273 | 114.67 | Yellow | 1688-89 | 141.67 | Grey |
| 428 | 115.17 | Yellow | 1690-91 | 141.62 | Grey |
| 610 | 118.34 | Yellow | 1692-93 | 141.67 | Grey |
| 768 | 126.68 | Yellow | 1694-95 | 141.7 | Grey |
| 944 | 127.88 | Yellow | 1696-97 | 141.67 | Grey |
| 1008 | 143.97 | Yellow | 1698-99 | 141.02 | Grey |
| 1140 | 148.25 | Yellow | 1700-01 | 141.53 | Grey |
| 1352 | 151.48 | Yellow | 1702-03 | 141.15 | Grey |
| 1504 | 152.12 | Yellow | 1704-05 | 141.59 | Grey |
| 1584 | 153.18 | Yellow | 1706-07 | 141.52 | Grey |
| 1666-67 | 154.59 | Yellow | 1708-09 | 141.53 | Grey |
| 1668-69 | 152.52 | Yellow | 1629 | 141.7 | Grey |
| 1670-71 | 151.65 | Yellow | 1323 | 141.98 | Grey |
| 1672-73 | 149.12 | Light yellow | 1115 | 141.12 | Grey |
| 1674-75 | 146.11 | Light yellow | 925 | 141.57 | Grey |
| 1676-77 | 144.01 | Grey | 809 | 141.12 | Grey |
| 1678-79 | 144.82 | Grey | 461 | 141.24 | Grey |
| 1680-81 | 143.87 | Grey | 183 | 141.12 | Grey |
| 1682-83 | 142.87 | Grey | | | |

Fig. 2 shows the curve obtained by plotting the average atomic weights of the fractions against the positions of the fractions in the plan of fractionation.

It appears from these results that the average atomic weights remained almost constant at a value between 141 and 142 in all of the fractions removed from fractionation at the insoluble end, and throughout the less soluble fractions in the final series up to fraction 1684-85. From this point the atomic weights rose to a maximum value of 154.59 in fraction 1666-67, fell rapidly to a minimum value of 114.67 in fraction 278, and rose again slightly in fractions 136 and 58. By far the greater portion of the material was contained in the portions with an almost constant atomic weight of about 141.

In the examination of the absorption spectra of the earths from the various fractions, neutral solutions of the chlorides of equal concentrations were used. Weighed amounts of the oxides from the various fractions were dissolved in hydrochloric acid, the acid being added very gradually

until the oxides just dissolved on boiling. The approximately neutral solutions of the chlorides of the rare earths thus obtained were diluted with water until each cubic centimeter contained 0.2 g. of the oxides and were then transferred to glass boxes 55 mm. in width. The absorption spectra were examined by means of a Krüss spectroscope previously cali-

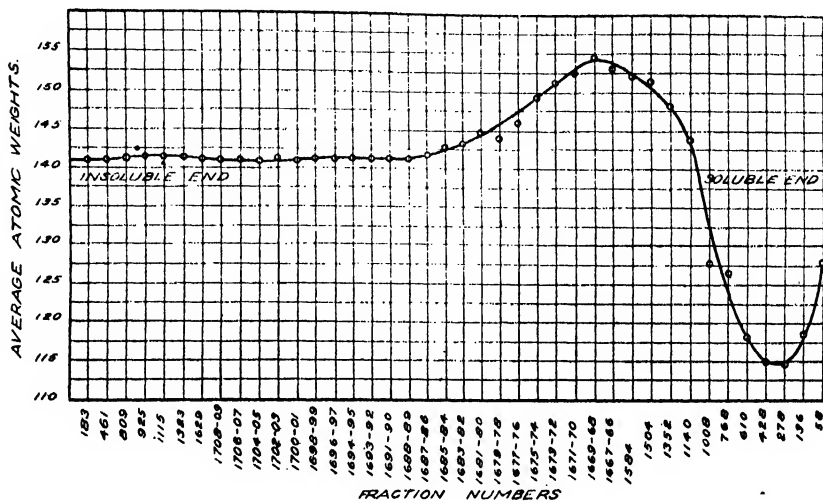


Fig. 2.

brated by the use of the Fraunhofer lines, the spectrum of the mercury arc, and the emission spectra of potassium, lithium, and thallium. A disc of zirconium oxide heated to incandescence in the oxyhydrogen flame was used as the source of light. In comparing the intensities of the absorption bands of the solutions of the rare earths from the various fractions, the apparatus devised by Dennis and Bennett was used.¹

In Fig. 3 are shown the curves obtained by plotting the relative intensities of the characteristic lines of the absorption spectra of neodymium, praseodymium, erbium, and holmium in the various fractions against the positions of the fractions in the plan of fractionation.

The general course of the separation may be traced by the examination of the results of the comparison of the absorption spectra and the determination of the average atomic weights of the earths from the end fractions and from the fractions of the final series. The high and constant concentration of praseodymium and neodymium in the less soluble fractions and the fact that these fractions have an average atomic weight of between 141 and 142 proves that the less soluble portions of the material consisted of a mixture of the elements of the didymium group and that little or no

¹ *Loc. cit.*

separation of the elements of this group had been effected. The increase of the concentrations of erbium and holmium beyond fraction 1678-79 explains the increase of the atomic weights to fraction 1584. That the atomic weights reached a maximum in fraction 1584 while the concentration of the erbium and holmium continued to increase until fraction 1008 was reached was probably due to the effect of the increasing concentration

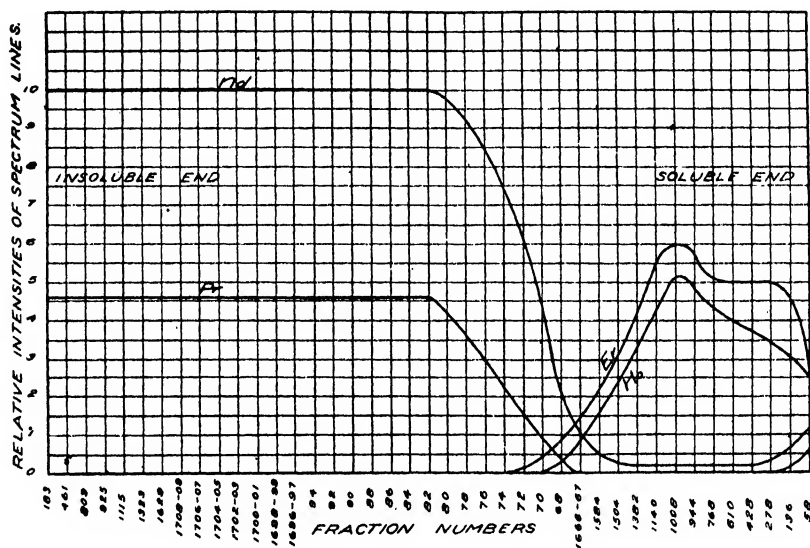


Fig. 3.

of yttrium in the more soluble fractions. The slight increase in the concentration of the neodymium and praseodymium in fractions 136 and 58 was in agreement with the rise in the atomic weight in these fractions and was due to the fact that they were removed from fractionation after comparatively few series of recrystallizations and therefore resembled more closely in composition the initial mixture of rare earths.

Dennis and Bennett, in their investigation of the fractional crystallization of the picrates of the rare earths, had observed a sudden and isolated concentration of neodymium and praseodymium in certain of the fractions of intermediate solubility. This observation was not confirmed in this present work. The earths of the didymium group were found to concentrate in the fractions at the insoluble end and in these fractions only. A portion of the material from one of the fractions of intermediate solubility from the final series of fractions obtained by Dennis and Bennett was analyzed and was found to contain considerable amounts of ammonium salts. Therefore it is probable that the results obtained by them in their work on the fractional crystallization of the picrates of the rare earths

were due to the fact that they were fractionating a complex mixture of the simple and the double ammonium picrates of the various earths. It is evident that the results of the fractional crystallization of such a mixture would be the results of two simultaneous, superimposed fractionations, and that each earth present would tend to concentrate in two or more separate regions of the final series of fractions.

The fractional crystallization of the picrates does not give an efficient separation of the individual elements of the didymium group. The ratio of the intensity of the neodymium spectrum to the intensity of the praseodymium spectrum remains approximately constant throughout all of the fractions. As a method for the separation of the didymium group from the yttrium and erbium groups, however, the fractionation of the picrates promises very good results. About 200 g. of the oxides of the yttrium and erbium groups was obtained from the more soluble fractions, although no trace of erbium or holmium bands could be detected in the absorption spectrum of the original material. Even after a comparatively short series of recrystallizations, the mother liquor at the soluble end showed a marked increase in the concentration of erbium and holmium and a very great decrease in the concentration of neodymium and praseodymium. Therefore the picrate method should be especially useful for the separation of the elements of the didymium group from the other rare earths and for the isolation of the earths of the erbium or yttrium groups from material containing large amounts of the didymium elements. The fractional crystallization of the picrates also appears to afford a rapid method for the separation of the yttrium earths of the erbium group.

Summary.

A mixture of the picrates of the rare earths of the didymium group, containing small amounts of the elements of the yttrium and erbium groups, was subjected to 42 series of fractional crystallizations. The earths of the didymium group concentrated in the less soluble fractions, while the most soluble fractions showed a concentration of yttrium, and the elements of the erbium group accumulated in the fractions of intermediate solubility. No indications of a concentration of neodymium or praseodymium in any fraction of intermediate solubility were observed.

The fractional crystallization of the picrates does not effect a separation of the individual elements of the didymium group, but is an efficient method for removing small amounts of the elements of the erbium and yttrium groups from the earths of the didymium group and for separating yttrium from erbium and holmium.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CORNELL UNIVERSITY.]

ANHYDROUS HYDRAZINE. III. ANHYDROUS HYDRAZINE AS A SOLVENT.¹

BY T. W. B. WELSH AND H. J. BRODERSON.

Received January 18, 1915.

In 1873, Gore² determined the approximate solubilities of a large number of substances in liquid ammonia. That liquid ammonia is an ionizing solvent has been shown by Cady.³ Franklin and Kraus⁴ studied the solubility in liquid ammonia of a large number of elements, and of various organic and inorganic compounds.

Other inorganic substances⁵ which act as ionizing solvents include such compounds as water, liquid hydrogen cyanide, liquid sulfur dioxide, concentrated nitric acid, arsenic trichloride, arsenic tribromide, phosphorus oxychloride, antimony trichloride, thionyl chloride, sulfuryl chloride, dimethyl sulfate, chlorosulfonic acid, concentrated sulfuric acid, and sulfur dichloride.

Nonaqueous ionizing solvents have also been investigated by McIntosh,⁶ Archibald,⁷ Calvert,⁸ Walden,⁹ Garner,¹⁰ and Schlesinger.¹¹

That anhydrous hydrazine is a poor conductor of the electric current has been shown by Cohen and Lobry de Bruyn.¹² The solubilities of sodium chloride, sodium nitrate, potassium chloride, potassium bromide, potassium iodide, potassium nitrate, and barium nitrate in anhydrous hydrazine have been determined by de Bruyn.¹³ Welsh¹⁴ has shown that sodium hydrazide is soluble in anhydrous hydrazine. In the present paper, the solubilities of a large number of substances in anhydrous hydrazine have been approximately determined as a preliminary investigation to the study of chemical reactions in this solvent. The results of the present investigation are described under the following headings: (1) Materials

¹ For the previous articles of this series, see Hale and Shetterly, *THIS JOURNAL*, **33**, 1071-6 (1911); Welsh, *Ibid.*, **37**, 497-508 (1915). The experimental work of this article was completed in June, 1913.

² *Proc. Roy. Soc.*, **21**, 140 (1873).

³ *J. Phys. Chem.*, **1**, 707-13 (1897).

⁴ *Am. Chem. J.*, **20**, 820-36 (1898).

⁵ For a complete summary of the literature related to ionizing solvents up to 1902, see Walden, *Z. anorg. Chem.*, **29**, 371 (1902).

⁶ *Trans. Am. Electrochem. Soc.*, **21**, 121 (1912).

⁷ *THIS JOURNAL*, **29**, 665, 1416 (1907).

⁸ *Drude's Ann. Physik.*, **1**, 483 (1900).

⁹ *Ber.*, **32**, 2862 (1899); *Bull. Acad. St. Petersburg*, 1055-82 (1911).

¹⁰ *Am. Chem. J.*, **46**, 236-40 (1911).

¹¹ *THIS JOURNAL*, **33**, 1924-33 (1912).

¹² *Proc. Acad. Wetenschappen*, **5**, 551-6 (1903); *J. Chem. Soc.*, **84**, II, 405 (1903).

¹³ *Rec. trav. chim.*, **15**, 174-84 (1896).

¹⁴ *THIS JOURNAL*, **37**, 497-508 (1915).

Used; (2) Apparatus Employed; (3) General Procedure; (4) Table of Results; (5) Summary.

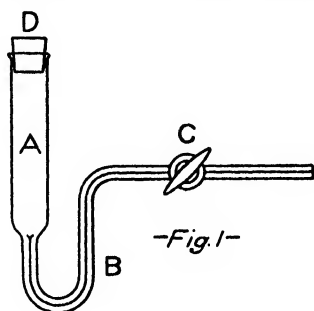
Materials Used.

The anhydrous hydrazine employed as solvent in the experimental work described in the following pages was prepared by first partially dehydrating commercial hydrazine hydrate with sodium hydroxide according to the method of Raschig.¹ Further removal of water was effected by treatment with barium oxide after the method of de Bruyn.² The form of distillation apparatus employed and the procedure followed in the respective distillations were those described by Welsh.³ The product was found on analysis to contain 99.7% hydrazine. The hydrazine was stored in 50 cc. sealed tubes. That no decomposition of hydrazine preserved in this way had taken place after a period of two years was shown by the fact that no appreciable increase in pressure could be noted when the containers were opened.

The solutes employed, with the exception of those noted below, were the ordinary pure chemicals of standard manufacture. Water of crystallization was removed wherever it was possible to accomplish this without decomposition. The salts of lanthanum, samarium, praseo- and neodymium which were employed were such as had been prepared during the course of certain investigations in this laboratory.

Apparatus Employed.

The solubility determinations were made in the form of apparatus shown in Fig. 1. The glass tube *A*, approximately 7 cm. in length and 1 cm. in diameter, was connected to a supply of pure, dry nitrogen through the capillary tube *B* and the stopcock *C*. During the course of an experiment, *A* was closed by means of the loosely fitting cork *D*, covered with tin foil. The action of the electric current upon the solutions was studied by means of the small platinum electrodes shown in Fig. 2. These electrodes, fused into the ends of glass tubes of small



¹ *Ber.*, **43**, 1927 (1910).

² *Rec. trav. chim.*, **14**, 458 (1895); **15**, 174-84 (1896); see also Hale and Shetterly, *THIS JOURNAL*, **33**, 1071-6 (1911).

³ *Loc. cit.*

TABLE I.

| Solutes. | Grams of solute dissolved in 1 cc. NH_4OH . | Action observed. | Phenomena ob- served at cathode. | Remarks. |
|--------------------------------|---|-------------------------------|-------------------------------------|---|
| Aluminum..... | .. | | | Insoluble |
| Aluminum chloride..... | 0.01 | None | Gas | M. C. |
| Aluminum iodide..... | .. | Gas evolved, slight explosion | | G. C. Decomp. |
| Ammonium bromide..... | 1.10 | NH_3 evolved | Gas | G. C. (de Bruyn, <i>Loc. cit.</i>) |
| Ammonium chloride..... | 0.75 | NH_3 evolved | Gas | Decomp. |
| Ammonium nitrate..... | 0.78 | NH_3 evolved | Gas | G. C. Decomp. |
| Ammonium oxalate..... | 0.44 | NH_3 evolved | Gas | G. C. Decomp. |
| Tertiary ammonium phosphate... | 0.00 | None | Gas | Slightly conducting. No de- comp. |
| Ammonium meta-vanadate..... | 0.02 | Brown ppt. and brown soln. | Gas | P. C. Slight decomp. |
| Antimony..... | 0.00 | None | Gas | Insoluble |
| Antimony trioxide..... | 0.01 | Brown soln. | Gas | P. C. Partially decomp. |
| Antimony oxychloride..... | 0.01 | None | Gas | M. C. |
| Antimony pentasulfide..... | 0.00 | White ppt. | Gas | P. C. |
| Arsenious acid..... | 0.01 | Black ppt. | Black deposit | P. C. Decomp. |
| Barium chloride..... | 0.31 | None | Gas | G. C. |
| Barium nitrate..... | 0.03 | None | Gas | G. C. (de Bruyn, <i>Loc. cit.</i>) |
| Barium oxide..... | 0.00 | None | Gas | P. C. |
| Barium sulfate..... | 0.00 | None | Gas | P. C. |
| Bismuth chloride..... | 0.32 | Black ppt. | Gas | See discussion of results |
| Boric acid..... | 0.55 | None | Gas | M. C. |
| Boron nitride..... | 0.00 | None | Gas | P. C. |
| Cadmium bromide..... | 0.40 | None | Black deposit | M. C. |
| Cadmium carbonate..... | 0.00 | None | Gas | P. C. |
| Cadmium iodide..... | 0.84 | None | Black deposit | G. C. |
| Cadmium sulfide..... | 0.00 | None | Gas | P. C. |
| Calcium..... | .. | None | | Insol. Dissolves on add. of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ |

| | | | | | |
|------------------------------------|------|-----------------------------|-----------------------------|-------|---|
| | 0.01 | None | Slight grey deposit | P. C. | |
| n chloride..... | 0.16 | None | Slight grey deposit | G. C. | White needlelike cryst. on standing |
| Calcium oxide..... | 0.00 | None | Gas | P. C. | |
| Cerous chloride..... | 0.03 | Gas | Reddish brown deposit | M. C. | |
| Cerous ammonium nitrate..... | 0.00 | White suspens | Gas | P. C. | Slight brown ppt. in solution |
| Cerous sulfate..... | 0.00 | Gas | Gas | P. C. | |
| Chromium chloride (anhydrous)..... | 0.13 | Gas, red soln. | Gas | G. C. | See discussion of results |
| Chromium sesquioxide..... | 0.00 | Gas | Gas | P. C. | Slaking action |
| Chromium trioxide..... | 0.01 | Gas. | Gas | P. C. | |
| Cobalt acetate..... | 0.01 | Black ppt. | Brown deposit | M. C. | |
| Cobalt chloride..... | 0.01 | Gas. Brown soln. | Black deposit | P. C. | |
| Copper..... | .. | | | | Insoluble on addition of $N_2H_4.H_2SO_4$ |
| hydrogen arsenite..... | 0.00 | Black ppt. Brown soln. | Brown deposit sol. in HCl | P. C. | Cu and As are probably precipitated |
| Copper chloride..... | 0.05 | Brown soln. Brown ppt. | Red deposit sol. in HNO_3 | G. C. | |
| Copper nitrate..... | 0.01 | Black ppt. | Red deposit | P. C. | |
| Copper sulfate..... | 0.02 | Black ppt. | Black deposit | G. C. | |
| Copper sulfide..... | 0.00 | Brown ppt. | Brown deposit | P. C. | |
| Ferrous sulfate..... | 0.01 | Gas, yellow ppt. | Black deposit sol. in HCl | | |
| Ferrous sulfide..... | 0.09 | Gas. Green soln. | Black ppt., sol. in HCl | P. C. | |
| Lead acetate..... | 0.00 | Black ppt. on standing | Black ppt. | P. C. | |
| Lead fluoride..... | 0.06 | Gas. Black ppt. on standing | Black ppt. | G. C. | |
| Lead metaborate..... | 0.02 | None | Black ppt., sol. in HCl | P. C. | |
| Lead chloride..... | 0.03 | Black ppt. | Black ppt., sol. in HCl | G. C. | |
| Lead iodide..... | 0.02 | Gas. Black ppt. | Black ppt., sol. in HCl | P. C. | |
| Lead nitrate..... | 0.52 | Yellow ppt. | Black deposit, sol. in HCl | G. C. | |

TABLE I (continued).

| Solutes. | Grams of solute dissolved in 1 cc. N_2H_4 . | Action observed. | Phenomena ob- served at cathode. | Remarks. |
|-------------------------------|---|-----------------------------|-------------------------------------|---|
| Red lead | 0.01 | None | Black deposit, sol. in HCl | P. C. |
| Lithium | .. | Slightly soluble | | More sol. on add. of $\text{N}_2\text{H}_4, \text{H}_2\text{SO}_4$ |
| Lithium carbonate | 0.00 | None | Gas | P. C. |
| Lithium chloride | 0.16 | None | White deposit, prob- ably solute | M. C. White deposit on anode, probably solute |
| Magnesium (powder) | .. | None | | Insol. Dissolves on addn. of $\text{N}_2\text{H}_4, \text{H}_2\text{SO}_4$ |
| Magnesium (ribbon) | .. | None | | Insol. Dissolves on addn. of $\text{N}_2\text{H}_4, \text{H}_2\text{SO}_4$ |
| Magnesium carbonate | 0.00 | None | Slight white deposit | P. C. |
| Magnesium chloride | 0.02 | Flocculent ppt. on standing | Slight white deposit | G. C. |
| Magnesium nitride | 0.00 | None | Gas | P. C. |
| Magnesium phosphate | 0.00 | None | Gas | P. C. |
| Magnesium sulfate | 0.00 | None | Slight white deposit | P. C. |
| Manganese | 0.00 | None | Gas | Insoluble |
| Manganese chloride | 0.13 | None | Black deposit, sol. in HCl | G. C. |
| Manganese sulfate | 0.01 | None | Black deposit | P. C. |
| Mercury | .. | .. | Black deposit | Insoluble |
| Mercurous acetate | 0.02 | Hg ppt. | Gas | M. C. |
| Mercurous chloride | 0.01 | Hg ppt. | Gas | M. C. |
| Mercurous nitrate | 0.02 | Hg ppt. | Gas | M. C. |
| Mercuric chloride | 0.01 | Hg ppt. | Gas | M. C. |
| Mercuric iodide | 0.69 | Hg ppt. | Gas | G. C. |
| Mercuric oxide (yellow) | .. | Hg ppt. | Gas | G. C. |
| Mercuric sulfide | .. | None | Gas | P. C. |
| Nickel chloride | 0.08 | Violet soln. | Black deposit, sol. in HCl | G. C. |

| Nickel nitrate..... | 0.03 | Violet soln., black ppt. | Black deposit, sol. in HCl | M. C. |
|-----------------------------|------|-------------------------------|---------------------------------|---|
| Nickel sulfate..... | 0.00 | Salt assumes lavender color | Slight black deposit | P. C. $\text{NiSO}_4 \cdot 2\text{N}_2\text{H}_4$ probably formed |
| Potassium..... | .. | Explosion takes place at once | | |
| Potassium bichromate..... | 0.01 | Grey ppt. | Gas | P. C. |
| Potassium bromide..... | 0.60 | None | Gas | G. C. (de Bruyn, <i>Loc. cit.</i>). |
| Potassium chloride..... | 0.09 | None | Gas | M. C. (de Bruyn, <i>Loc. cit.</i>). |
| Potassium carbonate..... | 0.01 | None | Gas | P. C. |
| Potassium chromate..... | 0.01 | None | Gas | P. C. |
| Potassium iodate..... | 0.01 | Gas | Gas | P. C. |
| Potassium iodide..... | 1.75 | None | Gas | G. C. (de Bruyn, <i>Loc. cit.</i>). |
| Potassium ferricyanide..... | 0.02 | Gas, white residue | Gas | M. C. |
| Potassium nitrate..... | 0.14 | None | Gas | G. C. (de Bruyn, <i>Loc. cit.</i>). |
| Potassium permanganate..... | 0.02 | Gas, brown ppt. | Gas | P. C. |
| Potassium sulfate..... | 0.05 | None | Gas | M. C. |
| Silver chloride..... | 0.00 | Ag mirror | Gas | G. C. Decomp. |
| Silver nitrate..... | 0.01 | Gas, Ag mirror | Gas | M. C. |
| Sodium..... | .. | Soluble | | |
| Sodium acetate..... | 0.06 | None | White deposit, probably soluble | M. C. |
| Sodium bromate..... | 0.01 | Gas, yellow solution | Gas | P. C. |
| Sodium bromide..... | 0.37 | None | White deposit, probably soluble | G. C. |
| Sodium carbonate..... | 0.00 | None | Gas | P. C. |
| Sodium chlorate..... | 0.66 | None | White deposit, probably soluble | G. C. (de Bruyn, <i>Loc. cit.</i>). |
| Sodium chloride..... | 0.08 | None | Gas | G. C. |
| Sodium nitrate..... | 1.00 | None | White deposit, probably soluble | G. C. (de Bruyn, <i>Loc. cit.</i>). |
| Sodium iodide..... | 0.64 | None | White deposit, probably soluble | G. C. |

TABLE I (continued).

| Solutes. | Grams of solute dissolved in 1 cc. N_2H_4 . | Action observed. | Phenomena observed at cathode. | Remarks. |
|----------------------------|---|---------------------------------------|-----------------------------------|---|
| Sodium sulfate..... | 0.00 | None | White deposit, probably solute | P. C. |
| Strontium chloride..... | 0.08 | None | Gas | M. C. |
| Strontium nitrate..... | 0.05 | None | Gas | M. C. |
| Strontium sulfate..... | 0.00 | None | Gas | P. C. |
| Tin..... | .. | None | | Insol., even on addn. of $N_2H_4.H_2SO_4$ |
| Zinc..... | .. | None | | Insol. Dissolved slightly on addn. of $N_2H_4.H_2SO_4$ |
| Zinc acetate..... | 0.04 | White suspension | Grey deposit, sol. in HCl | M. C. |
| Zinc carbonate..... | 0.00 | White suspension | Gas | P. C. |
| Zinc chloride..... | 0.08 | None | Black deposit | G. C. |
| Zinc sulfate..... | 0.00 | White suspension | Grey deposit | P. C. |
| Zinc phosphate..... | 0.00 | None | Gas | P. C. |
| Zinc sulfide..... | 0.00 | None | Gas | P. C. |
| Iodine..... | .. | Gas explosion | Gas | |
| Lanthanum chloride..... | 0.00 | None | Slight deposit | M. C. |
| Neodymium chloride..... | 0.00 | None | Slight brown deposit, sol. in HCl | M. C. |
| Palladium chloride..... | 0.01 | Gas. Black ppt. | Black deposit | M. C. Decomp. |
| Platinic chloride..... | 0.01 | Black ppt. | Gas | M. C. Decomp. |
| Praseodymium chloride..... | 0.00 | None | Slight brown deposit | M. C. |
| Samarium sulfate..... | 0.01 | None | Slight white deposit | P. C. |
| Rubidium chloride..... | 0.03 | None | Gas | M. C. |
| Sulfur..... | 0.54 | Brown soln., H_2S and NH_3 formed | Gas | G. C. (de Bruyn, <i>Loc. cit.</i>) (Ephraim and Piotrowski, <i>Ber.</i> , 44, 386 (1911)) |

diameter, had an area of 32 sq. mm., were 4 mm. apart, and were mounted in a cork covered with tin foil and fitted to the tube *A*. The electrodes were connected to the source of current through a reversing switch, a voltmeter and a milliammeter, both of which could be temporarily cut out of the circuit. A number of solubility vessels were mounted on a wooden support and one pair of electrodes used interchangeably.

General Procedure.

The solubility vessels were thoroughly cleaned and dried, one cc. of anhydrous hydrazine introduced, and the vessel tightly corked. The finely powdered solute was then introduced in successive small portions taken from a weighed amount contained in a small glass bottle. Nitrogen was allowed to bubble slowly through the apparatus in order to provide thorough stirring, care being taken that the cork did not fit tightly enough to prevent the escape of gas. This procedure was continued until no more of the solute would dissolve. In the course of the experiments the solutions were closely observed for evolution of gas and other accompanying phenomena. The action of the electric current was then studied by removing the cork *D*, and substituting for it the cork supporting the electrodes, as previously described. In those cases where a noticeable deposit was formed on an electrode, the direction of the current was reversed and the effect upon the deposit was noted under these conditions. No great accuracy is claimed for the solubility determinations, as weighings were made only to the second place and the temperature was not kept constant, and furthermore, it was very difficult to prevent slight oxidation of the hydrazine taking place, and the introduction of slight amounts of moisture with the apparatus at hand. The chief object of the research has been to obtain qualitative and approximate quantitative data concerning the behavior of various substances toward hydrazine. In Table I the third column contains the results of observations upon the behavior of the substances when introduced into hydrazine. In the fourth and fifth columns are recorded chiefly the facts noted during electrolysis. The abbreviations "G. C.," "M. C.," and "P. C.," signify, respectively, that the solutions under consideration are good, medium, or poor conductors of the electric current. A four volt circuit was used and where the current was less than 15 m. amp. it was designated as "P. C.," between 15 and 50 m. amp. as "M. C.," and above 50 m. amp. as "G. C."

Summary.

The principal results of this investigation, the details of which have been recorded in the foregoing table, may conveniently be summed up under the following headings:

Elements.—Of the metallic elements employed, the alkali metals are the only ones that are appreciably acted upon and dissolved. The solubility increases with rise of atomic weight. Sulfur and iodine are both

very soluble and chemical decomposition of the solvent takes place with rapidity, especially in the latter case.

Halogen Compounds.—The solubility of these compounds appears to increase with the increase of atomic weight of the halogen. In the case of the alkaline earth metals, crystals separate out from the solutions on standing, which are probably hydrazinated salts.¹ This was especially noticeable in the case of calcium chloride. The iodides are much more readily soluble than the corresponding bromides.

Carbonates.—The carbonates are insoluble or at most only very slightly soluble.

Oxides.—The oxides are apparently all insoluble.

Nitrates.—The nitrates, with the exception of those which react with the solvent, are in the majority of cases soluble.

Sulfates and Sulfides.—Both of these classes of compounds are only slightly soluble.

Ammonium Compounds.—These are all soluble with the exception of tertiary ammonium phosphate. Solution is accompanied by the evolution of large amounts of ammonia gas. Liberation of ammonia from ammonium salts by the action of free hydrazine has already been noted by de Bruyn.² This process, which is essentially one of *hydrazinolysis*, is the reverse of the decomposition of hydrazine salts in liquid ammonia already studied in this laboratory.³

Bismuth Compounds.—Bismuth chloride dissolves and reacts with the solvent, giving a quantitative precipitation of metallic bismuth.

Cadmium Compounds.—The carbonate and sulfide are insoluble. The halogen compounds are very soluble without visible chemical action.

Miscellaneous Compounds.—The mercury compounds, with the exception of mercuric sulfide which is insoluble, react chemically with the solvent immediately on being introduced, with formation of metallic mercury.

It is very probable that nickel and cobalt compounds are dissolved and react chemically with the solvent giving hydrazine addition products. In the case of cobalt chloride, a slow continuous decomposition was noticed with formation of a cobalt mirror on the tube.

The copper and lead compounds are all soluble with more or less decomposition. With the silver salts, the formation of a silver mirror was noted in each case.

This investigation was undertaken at the suggestion of Professor A. W. Browne and was carried out in cooperation with him.

ITHACA, N. Y.

¹ Curtius and Schrader, *J. prakt. Chem.*, [2] 50, 311.

² *Loc. cit.*

³ Browne and Welsh, *THIS JOURNAL*, 33, 1728 (1911); Browne and Houlehan, *Ibid.*, 33, 1734 (1911); Friedrichs, *Ibid.*, 35, 244 (1913); *Z. angew. Chem.*, 26, 201 (1913).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CORNELL UNIVERSITY.]

ANHYDROUS HYDRAZINE. IV. CHEMICAL REACTIONS IN ANHYDROUS HYDRAZINE.¹

BY T. W. B. WELSH AND H. J. BRODERSON.

Received January 18, 1915.

Considerable attention has been given to the study of chemical reactions in nonaqueous inorganic solvents by a number of investigators. The most important work as related to the present investigation was that carried out by Franklin and his associates upon liquid ammonia.² The behavior of hydrazine sulfate in liquid ammonia has been studied by Browne, Welsh, and Houlchan,³ and by Friedrichs⁴ who showed that ammonolysis took place with formation of free hydrazine and ammonium sulfate.

That sulfur dioxide will act as a solvent and also as a medium in which chemical action may take place has been shown by Walden⁵ and his associates, and also by Franklin.⁶ Investigations of reactions in organic solvents have been carried on by Naumann,⁷ Kahlenberg,⁸ Kahlenberg and Schmidt,⁹ Matthews,¹⁰ Gates,¹¹ and Barneby.¹²

Franklin has shown that the acids of the ammonia system are the acid amides and imides, including the amides and imides of the nonmetallic elements. The bases are the metallic amides and imides and the salts the metallic derivatives of the amides and imides. In an analogous man-

¹ For the previous articles of this series see Hale and Shetterly, *THIS JOURNAL*, 33, 1071-6 (1911); Welsh, *Ibid.*, 37, 497-508 (1915); Welsh and Broderson, *Ibid.*, 37, 816. The experimental work of this article was completed in June, 1913.

² See Franklin and Kraus, *Am. Chem. J.*, 20, 820, 836 (1898); 21, 14 (1899); 23, 277 (1900); *THIS JOURNAL*, 27, 191 (1905); *J. Phys. Chem.*, 11, 553 (1907); Franklin and Stafford, *Am. Chem. J.*, 28, 83 (1902); Franklin and Cady, *THIS JOURNAL*, 26, 499 (1904); Franklin, *THIS JOURNAL*, 27, 820-51 (1905); 29, 35 (1907); *Z. physik. Chem.*, 69, 272 (1909); *Am. Chem. J.*, 47, 285, 361 (1912); *Orig. Comm. 8th Intern. Cong. Appl. Chem.*, 2, 103; 6, 119-30, 1410 (1912); Franklin and Hine, *THIS JOURNAL*, 34, 1497, 1501 (1912). See also Browne and Holmes, *THIS JOURNAL*, 35, 672-81 (1913); Kraus and Bray, *Ibid.*, 35, 1315-1434 (1913); Cady and Lichtenwalter, *Ibid.*, 35, 1434-40 (1913); Kraus, *Ibid.*, 36, 864-77 (1914).

³ *THIS JOURNAL*, 33, 1728, 1734 (1911).

⁴ *Ibid.*, 35, 244 (1913); *Z. angew. Chem.*, 26, 201 (1913).

⁵ *Ber.*, 32, 2865 (1899); *Z. anorg. Chem.*, 25, 209 (1900); 29, 371 (1902); Walden and Centnerzwer, *Ibid.*, 30, 145 (1902); *Z. physik. Chem.*, 39, 513 (1902); Centnerzwer and Teleton, *Z. Elektrochem.*, 9, 799-802 (1903); *J. russ. phys. chem. Ges.*, 36, 62-71 (1904).

⁶ *J. Phys. Chem.*, 15, 675-97 (1912).

⁷ *Ber.*, 32, 999 (1899).

⁸ *J. Phys. Chem.*, 6, 6 (1902); *Z. physik. Chem.*, 46, 63 (1903).

⁹ *J. Phys. Chem.*, 6, 447 (1902).

¹⁰ *Ibid.*, 9, 641 (1905).

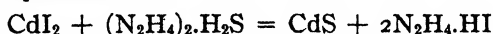
¹¹ *Ibid.*, 15, 97 (1911).

¹² *THIS JOURNAL*, 34, 1174-89 (1912).

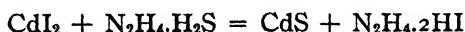
ner, the acid hydrazides, the metallic hydrazides and the metallic derivatives of the acid hydrazides may be considered, respectively, as acids, bases, and salts in the hydrazine system. The nitrides and tetrahydrazides may be considered as bearing the same relation to the ammonia and the hydrazine system, respectively, that the oxides bear to the aquo system of Lavoisier. Furthermore that the hydrazine salts of aquo acids, soluble in anhydrous hydrazine, will act as acids is indicated by the fact that they will discharge the color of phenolphthalein, and will dissolve certain metals that are insoluble in anhydrous hydrazine itself, with liberation of hydrogen. This is similar to the action of analogous ammonium salts in liquid ammonia.

The present paper is a preliminary report on the hydrazine system of acids, bases and salts, and contains a study of the action in anhydrous hydrazine solutions of: (a) hydrazine sulfide upon cadmium iodide; (b) hydrazine sulfide upon zinc chloride; (c) sodium hydrazide upon zinc chloride; (d) metallic sodium upon certain salts; (e) certain metals upon hydrazine sulfate; (f) metallic sodium and sodium hydrazide upon hydrazine chloride.

Action of Hydrazine Sulfide upon Cadmium Iodide in Anhydrous Hydrazine.—Since cadmium iodide is appreciably soluble and cadmium sulfide insoluble in anhydrous hydrazine, it could be reasonably supposed that hydrazine sulfide would precipitate cadmium sulfide from a solution of cadmium iodide in anhydrous hydrazine in accordance with either of the following equations:



or



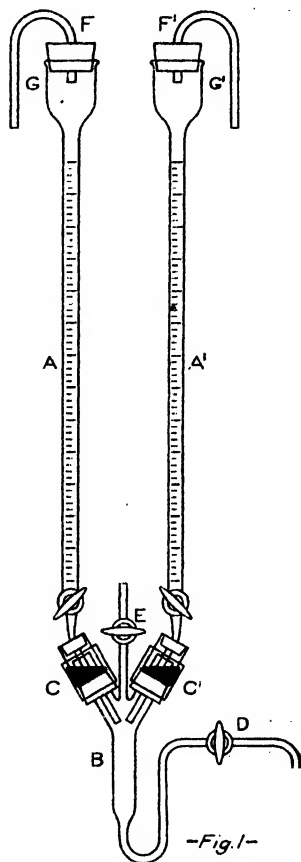
Ephraim and Peiotrowski¹ state that either $(\text{N}_2\text{H}_4)_2\cdot\text{H}_2\text{S}$ or $\text{N}_2\text{H}_4\cdot\text{H}_2\text{S}$ is formed when sulfur is dissolved in anhydrous hydrazine. The solution of hydrazine sulfide used in this experiment was prepared, therefore, by dissolving sufficient sulfur in anhydrous hydrazine to form a deep reddish yellow solution. A solution of cadmium iodide was prepared in the form of apparatus used in studying solubilities in anhydrous hydrazine.² The hydrazine sulfide solution was added to this, and a yellow precipitate of cadmium sulfide was formed, which on analysis was found to contain cadmium 74.6%, sulfur 22.8%. Theory for CdS, cadmium, 77.79%; sulphur, 22.21%.

In view of the fact that solutions of hydrazine sulfide are highly colored it was considered possible to titrate unknown solutions of such salts as zinc chloride and cadmium iodide, with standard solutions of the sulfide, using the disappearance of the color to indicate the end point of the

¹ *Ber.*, 44, 386 (1911); see also de Bruyn, *Rec. trav. chim.*, 13, 433 (1894).

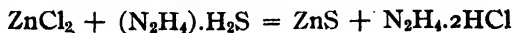
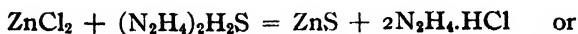
² See the preceding article.

reaction. In order to test the method in a preliminary way, the apparatus shown in Fig. 1 was devised. It consists of the two ten cubic centimeter burets *A* and *A'* with long curved tips reaching into the vessel *B*. The joints *C* and *C'* are made tight by means of mercury seals. The vessel *B* is connected with a source of pure, dry nitrogen which could be bubbled through the liquid contained in *B* at any desired speed by regulating the stopcock *D*, and then be allowed to escape into the atmosphere through stopcock, *E*. Oxidation of the solutions contained in the burets *A* and *A'* was prevented by keeping them in an atmosphere of nitrogen introduced through the tubes *F* and *F'*, held in place by the corks *G* and *G'*, which were completely encased in tin foil.



Solutions of hydrazine sulfide and cadmium iodide were prepared by dissolving weighed amounts of sulfur and cadmium iodide, respectively, in a known volume of anhydrous hydrazine. The hydrazine sulfide contained 0.039 g. of sulfur per cc. and the cadmium iodide solution 0.27 g. cadmium iodide per cc. A measured amount of the hydrazine sulfide solution was introduced into *B*, nitrogen was slowly bubbled through this in order to provide stirring, and cadmium iodide solution was slowly run in until the yellow color of the sulfur solution disappeared. It was found that 3.3 cc. of cadmium iodide solution completely discharged the yellow color from 2 cc. of the hydrazine sulfide solution. The calculated amount of cadmium iodide solution for 2 cc. of hydrazine solution was 3.2 cc.

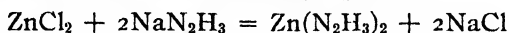
Action of Hydrazine Sulfide upon Zinc Chloride in Anhydrous Hydrazine.—The apparatus employed and the procedure were the same as were described in the preceding experiments. When a solution of zinc chloride was added to a solution of hydrazine sulfide a white precipitate of ZnS was obtained, probably in accordance with either of the following equations:



The precipitate was analyzed and was found to contain zinc 60.7%, and sulphur 28.3%. Theory for ZnS , zinc 67.1%, sulphur 32.9%.

A solution of hydrazine sulfide containing 0.039 g. sulfur per cc. was titrated against a solution of zinc chloride containing 0.098 g. per cc. It was found that 3.3 cc. of the zinc chloride solution would discharge the color from 1.9 cc. of the sulfide solution. The calculated amount of zinc chloride solution for 1.9 cc. sulfide solution is 3.26 cc.

Action of Sodium Hydrazide on Zinc Chloride in Anhydrous Hydrazine.—Ebler and Krause¹ prepared zinc hydrazide by the action of zinc ethyl or zinc diamide on a suspension of hydrazine in anhydrous ether, and suggest these methods as generally applicable for the preparation of metallic hydrazides. It was thought that zinc hydrazide might be precipitated in hydrazine by the action of sodium hydrazide on zinc chloride in accordance with the following equation:



which would be analogous to the precipitation of zinc hydroxide by sodium hydroxide in aqueous solution. A preliminary study of this reaction was made in the apparatus described in Fig. 1. Approximately equivalent solutions of sodium hydrazide and zinc chloride were employed. The yellow color of sodium hydrazide solution was immediately destroyed on coming into contact with zinc chloride solution and a white flocculent precipitate, probably zinc hydrazide, was immediately formed. This precipitate seemed to be insoluble in an excess of sodium hydrazide but was dissolved in an excess of zinc chloride solution. Satisfactory analyses of the product could not be obtained both because of the small amount of the product and because of the difficulty in removing the last trace of hydrazine without decomposition. This solubility of zinc hydrazide in a hydrazine solution of zinc chloride is analogous to the solubility of zinc hydroxide in a water solution of zinc chloride.

Action of Metallic Sodium on Solutions of Certain Salts in Anhydrous Hydrazine.—A preliminary study was made of the action of metallic sodium upon solutions of cadmium iodide, zinc chloride, magnesium chloride, calcium chloride, barium chloride, and ferric sulfate in anhydrous hydrazine.

About 10 cc. of a saturated solution of cadmium iodide in a solubility tube was treated successively with small amounts of metallic sodium. The action proceeded fairly rapidly with the formation of a finely divided black precipitate, undoubtedly metallic cadmium. In contact with water the precipitate became superficially coated with a white material, probably cadmium hydroxide, which, when treated with a small amount of dilute hydrochloric acid, was dissolved, leaving at first the black finely divided cadmium which finally reacted with the acid with evolution of gas. The black precipitate oxidized very readily in the air, and even during the process of drying the moist product at 150° in an atmosphere of hydrogen,

¹ *Ber.*, 43, 1690-5 (1910).

oxidation took place with formation of small amounts of yellow and green oxides.

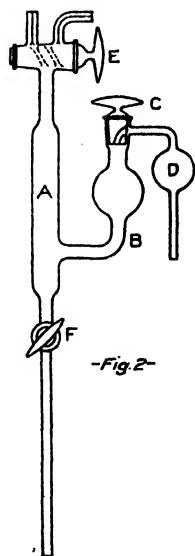
When a solution of zinc chloride was treated with metallic sodium a finely divided black precipitate was produced which was very easily oxidized in the presence of air or moisture. The material, after being dried in hydrogen at 200° , was decidedly metallic and showed traces of zinc oxide. No satisfactory analyses could be made because of the small amount of precipitate obtained, but the substance was undoubtedly metallic zinc in finely divided form.

When a solution of ferric sulfate was treated with metallic sodium, a black precipitate was formed which, after being washed with alcohol and water, was found to be soluble in hydrochloric acid with evolution of gas. Qualitative tests of this solution showed the presence of iron and the absence of hydrazine and sulfuric acid, showing that the precipitate was in all probability metallic iron.

When saturated solutions of the chlorides of magnesium, calcium or barium were treated with metallic sodium, chemical action took place and ceased when the sodium became coated with a white material. When this was removed by scraping with a glass rod, the action again commenced and continued until the metal was again coated. Since metallic magnesium calcium and barium in the finely divided state react with anhydrous hydrazine in the presence of hydrazine salts, these metals would not be expected to precipitate as do cadmium, zinc and iron. The white coating on the sodium was probably sodium chloride.

Action of Certain Metals upon a Solution of Hydrazine Sulfate in Anhydrous Hydrazine.—The behavior of zinc, copper, tin, aluminum, magnesium, calcium, and lithium toward anhydrous hydrazine and toward solutions of hydrazine sulfate in anhydrous hydrazine was studied with the apparatus shown in Fig. 2. This consisted of the tube *A* of about 10 cc. capacity with the side arm *B*, which was formed with a bulb of slightly greater capacity than tube *A*. The glass stopper *C* could be removed for the purpose of introducing solid material or of connecting the tube *B* with the tube *D*, which was connected with a mercury trap, not shown in the sketch. Communication could be established between *A* and either a Hempel buret or a suction apparatus by means of a two-way stopcock *E*. The stopcock *F* served for the introduction of hydrazine by means of suction or for the withdrawal of a sample during the course of the experiments.

The behavior of zinc upon anhydrous hydrazine was



studied in the following manner: the apparatus was evacuated, tube *A* was filled with anhydrous hydrazine drawn in through the stopcock *F*, stopcock *C* was then withdrawn and about 0.02 g. of zinc was introduced through the side arm *B*. Stopcock *C* was then turned to make connection with *D*. No measurable amount of gas was evolved. About 0.06 g. of hydrazine sulfate was introduced through *C* but no action was observed to take place. Even in contact with small pieces of platinum foil the zinc showed no tendency to dissolve. Metallic copper, tin, and aluminum, respectively, were similarly introduced, but were found to be without action upon either the hydrazine or the solution of hydrazine sulfate in hydrazine. Magnesium and calcium showed no tendency to dissolve in hydrazine or to react with it, while lithium slowly went into solution with evolution of gas. On the addition of hydrazine sulfate, however, gas was rapidly evolved in each case until the metal became coated with a white deposit which in all probability consisted of the sulfate. This coating could be partially removed by shaking, whereupon gas was again evolved until the metal became recoated. Shaking was continued from time to time until no further evolution of gas could be induced. The gases were analyzed in each case and were found to consist solely of hydrogen and nitrogen, the former in rather larger amounts than the latter. The presence of nitrogen in the gases evolved from hydrazine, when acted upon by certain metals, recalls the work of Turrentine and Moore¹ who have found that by the action of metallic copper upon hydronitric acid in aqueous solution nitrogen and ammonia were formed. Hydrazine under these conditions may therefore be considered to act virtually as an oxidizing or more strictly a nitridizing² agent. The reduction of hydrazine (hydrogen dinitride) with formation of ammonia and nitrogen would obviously be analogous to the reduction of hydrogen dioxide with the formation of water and oxygen. Magnesium was used both in the form of ribbon and powder. The action of the powder was much more rapid and complete than that of the ribbon. From the above results hydrazine sulfate can be regarded as acting as an acid in anhydrous hydrazine solution. This action is analogous to that of an ammonium salt in liquid ammonia.³

Action of Metallic Sodium and a Solution of Sodium Hydrazide upon Solutions of Hydrazine Chloride in Anhydrous Hydrazine.—Hydrazine monochloride was prepared according to the method described by Curtius and Schulz.⁴

The action of sodium upon a solution of hydrazine chloride was studied in one of the solubility tubes described in the preceding article. A strong

¹ THIS JOURNAL, 33, 382-4 (1912).

² See Browne and Welsh, THIS JOURNAL, 33, 1728 (1911).

³ Franklin, *loc. cit.*; see also Browne and Houlehan, THIS JOURNAL, 33, 1734 (1911).

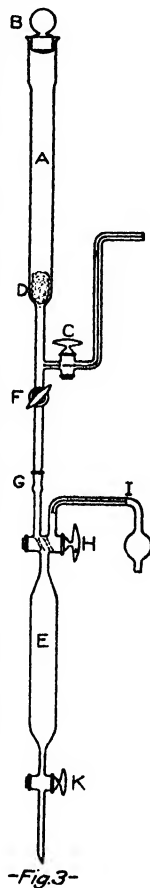
⁴ J. prakt. Chem., [2] 42, 520 (1890).

solution of hydrazine chloride was placed in the tube and metallic sodium was added in successive small quantities. The sodium floated on the surface of the solution and reacted slowly. A white crystalline precipitate was formed which, after it had accumulated in sufficient quantity, was filtered in a Gooch crucible, washed with 95% alcohol, dried, and heated to dull redness on platinum foil to remove any hydrazine chloride. This material was dissolved in a measured volume of water and aliquot portions were analyzed for sodium and chlorine. The sodium was determined as sodium sulfate and the chlorine was titrated with ammonium thiocyanate. The results of the analyses of the two samples were: Na (1) 39.12%, (2) 39.03%; Cl (1) 60.41%, (2) 60.03%. Theory for NaCl: Na 39.34%, Cl 60.66%.

The action of sodium hydrazide upon hydrazine chloride was next studied. In order to prepare and keep a sufficient amount of sodium hydrazide solution, the apparatus shown in Fig. 3 was devised. It consisted of a mixing tube, *A*, closed by the glass stopper *B*, and connected with a supply of pure dry nitrogen through the capillary tube and stopcock *C*. The glass wool shown at *D* served to filter out any solid material when the solution was passed into the storage tube *E* which was connected with *A* through the stopcock *F* and the ground joint *G*. *H* is a two-way stopcock connecting either with *G* or with the capillary tube and bulb *I*. Stopcock *K* served for the withdrawal of portions of sodium hydrazide solution.

Sodium hydrazide was prepared in the following manner: a quantity of hydrazine was introduced into *A*, after air had been displaced from the entire apparatus by means of nitrogen introduced through *C*. While nitrogen was allowed to bubble through the liquid in *A*, successive portions of metallic sodium were introduced by removing stopper *B* which was prevented from fitting tightly by means of a piece of fine platinum wire hung over the lip. After the sodium had completely dissolved, the storage tube *E* was evacuated and the sodium hydrazide solution was introduced by proper manipulation of stopcocks *F* and *H*. The storage tube was then separated from the rest of the apparatus, the end of tube *I* was allowed to dip below the surface of mercury contained in a vessel not shown in the sketch, and the stopcock *H* adjusted so as to permit the escape of any gas that might be formed in *E* through *I* without danger of introduction of air.

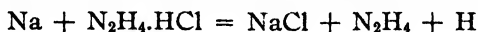
When solutions of sodium hydrazide and hydrazine chloride are mixed



-Fig. 3-

the yellow color of the sodium hydrazide is immediately discharged, provided that the hydrazine chloride is in excess. In order to obtain the sodium chloride, which did not precipitate from the rather dilute solutions employed, the resulting liquid was evaporated to dryness, and the residue was heated to drive off the excess of hydrazine chloride. Analysis of two samples of the solid residue gave the following results: Na (1) 39.53%, (2) 39.59%; Cl (1) 59.61%, (2) 60.15%. Theory for NaCl:Na 39.34%, Cl 60.66%.

The action of sodium and of sodium hydrazide upon hydrazine chloride in hydrazine solution may be expressed by means of the following equations:



and



Summary.

In the present investigation it has been shown :

1. That cadmium and zinc may be precipitated as sulfides (or hydrazinated sulfides) by the action of hydrazine sulfide on salts of these metals soluble in anhydrous hydrazine. It was also shown that the yellow color of the hydrazine sulfide could be made to serve as indicator in the titration of cadmium and zinc salts.
2. That a hydrazide of zinc is probably precipitated when sodium hydrazide acts upon zinc chloride in anhydrous hydrazine.
3. That metallic sodium will precipitate the metals cadmium, zinc, and iron from solutions of these salts in anhydrous hydrazine and that magnesium, calcium, and barium are not precipitated.
4. That zinc, copper, tin, and aluminum do not react with anhydrous hydrazine; but that magnesium, calcium, and lithium show a slight action.
5. That sodium chloride is formed by the action of either metallic sodium or a solution of sodium hydrazide on a solution of hydrazine chloride in anhydrous hydrazine.
6. That reactions may take place in anhydrous hydrazine similar to those that occur in water, in liquid ammonia and in certain other dissociating solvents.

A further study of reactions in anhydrous hydrazine solution with the special object in view of gaining information regarding the hydrazine system of acids, bases, and salts is now in progress in this laboratory and will be made the subject of a future communication.

This investigation was undertaken at the suggestion of Professor A. W. Browne and was carried out in coöperation with him.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE ATOMIC WEIGHT OF TANTALUM.

[SECOND PAPER.]¹

BY GEORGE W. SEARS AND CLARENCE W. BALKE.

Received February 18, 1915.

No very satisfactory agreement or concordance has been obtained in the investigations which have been carried out for the determination of the atomic weight of tantalum. In 1906 Hinrichsen and Sahlborn² published five determinations of the ratio $2Ta : Ta_2O_5$, but with a variation amounting to more than a unit in the atomic weight. Yet, these determinations, without doubt, were the most accurate up to that time. In 1910, Balke³ published a series of eight determinations of the ratio $2TaCl_5 : Ta_2O_5$, in which he obtained an average of 181.5 ± 0.098 for the constant, and in the following year Chapin and Smith,⁴ in a series of eight determinations of the ratio $2TaBr_5 : Ta_2O_5$, obtained 181.8 ± 0.199 .

Since both Balke, and Chapin and Smith must have had a very pure salt, and since its conversion to the oxide is attended with very little manipulation, it would seem that the principle involved is at fault. The object of this investigation, therefore, was to study the ratios $2TaCl_5 : Ta_2O_5$ and $TaCl_5 : 5Ag$, with respect to their values for the determination of the atomic weight of tantalum, as well as to establish a more accurate value of the constant if possible.

Preparation of Materials.

Chlorine.—The chlorine used throughout this investigation was prepared by allowing hydrochloric acid to drip upon potassium permanganate contained in a large flask. The acid used was prepared by distilling the constant boiling mixture from a large Jena retort. Small quantities of potassium permanganate were put in during the first part of the distillation, and the first portions of the distillate were rejected. The chlorine was passed through three towers filled with glass beads. In the first tower the beads were kept moist with water, while in the other two concentrated sulfuric acid was allowed to drip from time to time. To remove the last traces of moisture, the chlorine was finally passed through a tube about a half meter long, containing glass wool interspersed with phosphorus pentoxide. With the exception of two ground-glass joints at the generator, all the apparatus employed for the

¹ The work described in this paper furnished the basis for a thesis by Mr. Sears presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois.

² *Ber.*, 39, 2600 (1906).

³ *THIS JOURNAL*, 32, 1127 (1910).

⁴ *Ibid.*, 33, 1497 (1911).

preparation or use of chlorine or hydrogen chloride throughout this investigation was made continuous.

In order to make sure the chlorine would not be contaminated by the phosphorus pentoxide, the gas was passed for several hours through the above drying train into water, which was subsequently found to give no test for phosphorus.

Sulfur Monochloride.—This compound was prepared by passing a stream of chlorine over molten sulfur, which had been twice recrystallized from freshly distilled carbon disulfide. The apparatus was constructed in such a way that the sulfur monochloride could be redistilled directly from the receiver. The first portions of the distillate were rejected, and the final product distilled directly into sealing bottles through which a current of dry, filtered air had been passed to remove all traces of moisture.

Nitric Acid.—The nitric acid used was distilled from a quartz distilling flask, the middle third being collected in a quartz receiver and retained for use.

Water.—The ordinary distilled water was redistilled, after the addition of alkaline permanganate, from the still used in this laboratory for conductivity water.

Sodium Chloride.—Chemically pure sodium chloride was dissolved in water, filtered, precipitated three times with hydrogen chloride, then recrystallized from water, dried and fused in a platinum crucible in an electric furnace.

Sodium Hydroxide.—The sodium hydroxide used in the absorption flask, was prepared by electrolyzing a solution of Kahlbaum's sodium hydroxide, using a silver anode and a mercury cathode, arranged according to the manner of the Castner-Kellner process. This was found to contain no chloride when tested in the nephelometer.

Hydrofluoric Acid.—The ordinary C. P. hydrofluoric acid was distilled after the addition of small amounts of silver nitrate and potassium hydroxide. A platinum still and receiver were used and the middle portion was retained for use. The acid treated in this way gave no opalescence with silver nitrate.

Silver.—The silver used in this investigation was prepared in essentially the same manner as that used by Richards and Wells¹ in their work on the atomic weights of sodium and chlorine.

Chemically pure silver nitrate was recrystallized three times from nitric acid and reduced with ammonium formate, which had been prepared by distilling ammonia gas into redistilled formic acid until the solution was neutral or slightly acid. The silver was then fused in porcelain crucibles lined with pure carbon² in an electric furnace. The fused silver was cleaned

¹ *Pub. Carnegie Inst. Wash.*, No. 28 (1905).

² Richards and Wells, *Ibid.*, No. 28 (1905).

with sand, etched with nitric acid, carefully washed, dissolved in nitric acid, and again reduced with ammonium formate. This was washed by decantation, dried, and fused in porcelain crucibles lined with pure lime¹ in an electric furnace. It was then carefully cleaned with a bristle brush, etched with nitric acid, and electrolyzed, using a pure silver wire as cathode, the fused silver as anode, and silver nitrate, made by dissolving some of the fused silver in nitric acid, as the electrolyte. This electrolytic silver was carefully washed, dried, and again fused in the pure lime-lined boats in a tube furnace through which was passed hydrogen, prepared from zinc and hydrochloric acid, and purified by passing through wash bottles containing alkaline permanganate, silver sulfate, caustic potash and finally through tubes containing heated platinized quartz and glass wool interspersed with phosphorus pentoxide. The bars of silver thus obtained were carefully cleaned, etched with nitric acid and preserved in a desiccator over solid potassium hydroxide. Before weighing, these bars were cut into pieces, etched to the desired weight with nitric acid, carefully washed and dried by heating for several minutes to approximately 120°.

Tantalum Oxide.—Tantalum oxide free from chloride was prepared by once recrystallizing the potassium fluotantalate from pure water to which had been added a small amount of hydrofluoric acid prepared as above. The oxide obtained from this salt, as described below, was tested for chloride by dissolving it in dilute hydrofluoric acid, contained in a platinum dish, using just enough of the acid to obtain a clear solution, adding silver nitrate and allowing the solution to stand for two days. No precipitate could be detected.

Tantalum Chloride.—Potassium fluotantalate which had been prepared for the earlier investigation was used as the starting point for the preparation of tantalum chloride. The fluotantalate was placed in a platinum dish and covered with sulfuric acid which had been distilled from quartz. The mass was slowly heated till all the hydrofluoric acid had disappeared and sulfuric acid fumes had begun to come off freely. The mixture was then evaporated to dryness, transferred to a large rubber dish and washed by decantation with large amounts of pure water. The material was finally dried, placed in quartz crucibles and strongly ignited in an electric furnace. The apparatus used for the preparation of the chloride is shown in Fig. 1. About 30 g. of the tantalum oxide were placed in the tube F, by means of a funnel through D, and the apparatus sealed together at B, D, H, and I, so that it formed a continuous piece of glass through O. A stream of chlorine was passed through the apparatus by means of the tube A, for several hours, the entire apparatus being warmed with a free flame from time to time, in order to remove any traces of mois-

¹ Richards and Wells, *Pub. Carnegie Inst. Wash.*, No. 28 (1905).

ture that might be present. Sulfur monochloride was then introduced into the bulb E, through C, and heated to boiling, the oxide at the same time being heated to a temperature just below the softening point of the glass. The tantalum chloride formed, together with the excess of sulfur monochloride, collected in Bulb I. When all the oxide had been converted into chloride the excess of sulfur monochloride was driven through the ap-

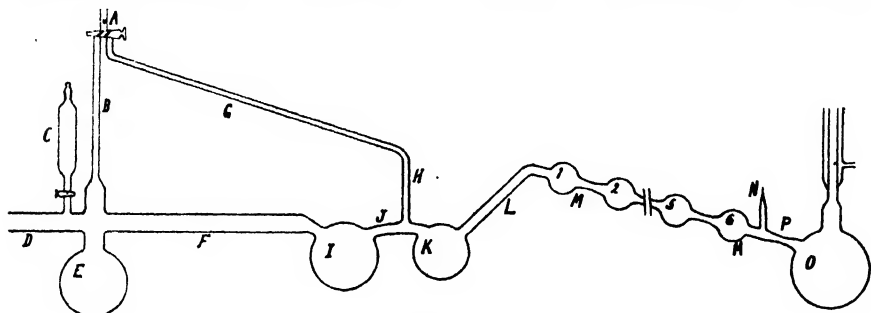


Fig. 1.

paratus and collected in O. The tantalum chloride was then distilled into K and the apparatus sealed off at J. The two-way stopcock A was then turned so that the chlorine passed through G. The tantalum chloride was then heated to boiling and kept at nearly that temperature while the remainder of the apparatus was heated so that any remaining sulfur monochloride and some tantalum chloride were driven over into O. The apparatus was then sealed off at P and, after cooling, at H.

Considerable difficulty was encountered during the process of distilling off the excess sulfur monochloride on account of a tendency of the mixture to explode. The force of these explosions varied considerably. Sometimes only a slight flash was noticed, but on several occasions the whole apparatus was destroyed. The explosions seemed to occur most frequently when the sulfur monochloride was practically all distilled over and the temperature raised to the boiling point of the tantalum chloride. It was also noticed that their occurrence depended on the rate at which the chlorine had been passed through the apparatus during the formation of the tantalum chloride. The more rapid the current, the less danger was there of an explosion. The cause of these explosions was not definitely determined, though it seems probable that they were due to a spontaneous combustion of the free sulfur which was always present in the mixture when a rapid current of chlorine was not kept up.

In order to replace the chlorine with dry air the tip N was broken off and quickly attached by means of a rubber cement to a glass tube leading through a two-way stopcock to two phosphorus pentoxide tubes, the bulbs M being heated previously in order to prevent the entrance of air when the tip N was broken off. The apparatus was then evacuated by means of

a good water pump attached to one of the pentoxide tubes. The two-way stopcock was then turned and air was allowed to enter slowly through the other pentoxide tube to which a wash-bottle containing sulfuric acid had been attached. This process was repeated until all the chlorine was replaced with dry air. The tantalum chloride was then heated to the boiling point while air was being drawn slowly from the apparatus. After cooling, the evacuation process was continued for two or three times, after which the tantalum chloride was distilled into the small bulbs M, and each sealed off for analysis. The chloride in these bulbs was pure white.

Experimental.

Ratio : $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$.—In order to test this ratio the purified chloride was transferred from the sealed bulbs to the quartz reaction flask shown in Fig. 2. The transfer in this and all succeeding cases was made as follows: By means of a knife and a hot file a crack was drawn about two-thirds around the neck of the bulb containing the chloride. This, together with the weighed flask, into the mouth of which had been inserted a wide necked funnel, was introduced into an air-tight box, provided with a removable glass top and a pair of rubber gloves fitted into two holes in the sides of the box. In order to insure a perfectly dry atmosphere, dishes containing pumice stone moistened with sulfuric acid were kept in the box and a stream of dry filtered air was passed through it for several hours before the transfer was made. By slipping the hands into the rubber gloves it was possible to break the neck off the bulb and transfer the chloride to the reaction flask without soiling the neck of the flask. After replacing the stopper it was removed from the box and again weighed.

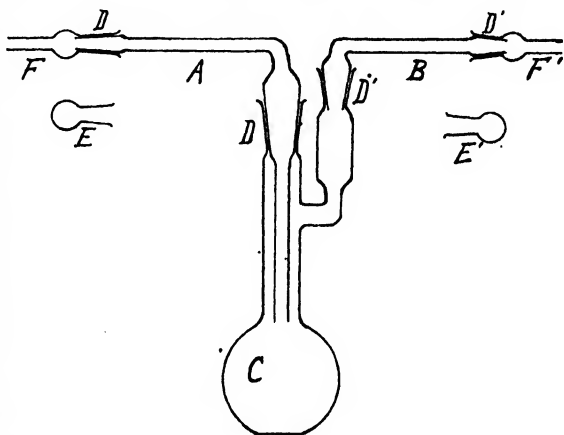


Fig. 2.—A, B, and C are fused transparent silica, D, D', D'', are carefully ground joints. Caps E, E', and tubes F, F', are made of soft apparatus glass.

The flask was then connected through an absorption train to an aspirating bottle in such a way that a slow current of moist air was drawn through it for several hours. Then water and a few drops of nitric acid were added and the tantalum oxide evaporated to dryness. The evaporation was repeated two or three times, after which the oxide was ignited

to bright redness. This was done by means of an electric resistance furnace made by winding Ni-chrome wire around an unglazed porcelain cup and insulating with powdered magnesia. By use of a rheostat the temperature was gradually increased to 900° to 1000° . During the ignition a very slow current of dry filtered air was drawn through the flask.

Three determinations were made in this way, but in no case could a constant weight be obtained, though in one case sixteen ignitions of about two hours each were made. On close examination a fine deposit was found in the exit tube, which showed that some of the oxide was being lost, either by volatilization or by being mechanically carried over by the slow current of air that was drawn through the flask. The latter seemed the more probable. In order, however, to test this point two more determinations were carried out in the same way, with the exception that no air was passed through the flask after evaporating to dryness. In the first, after eight ignitions of a half hour each a fairly constant weight was obtained, but on examining the exit tubes a fine deposit was quite noticeable. In the second, nineteen ignitions of a half hour each were made without obtaining a constant weight. The loss during any one ignition varied from a few hundredths to almost a milligram. A fine, white deposit was found in the exit tubes in this determination also.

The result of these two series showed quite conclusively that it would be impossible to obtain a satisfactory ratio by trying to hydrolyze the chloride and ignite to the oxide, since the result depended wholly on the time of heating, a fact which might have escaped detection if the reaction flask had not been supplied with the horizontal exit tubes. In order to determine more satisfactorily the reason for this, the following experiment was carried out: A sample of tantalum chloride was carefully hydrolyzed and evaporated with nitric acid two or three times and finally ignited in the quartz flask, Fig. 2, for two hours in the electric furnace. A part of the resulting oxide was then removed from the flask and fused with potassium pyrosulfate. The gases present in the mixture were at the same time conducted into a solution of silver nitrate. No opalescence in the silver solution was detected, though the melt was boiled for some time after a clear fusion had been obtained. From this it was assumed that the tantalum oxide contained no chloride. The remainder of the tantalum oxide in the flask was weighed and ignited for two-hour periods. The following weights were obtained: 1.2256, 1.2241, 1.2240. A little nitric acid was then added and the mixture evaporated to dryness and ignited for one-hour periods. The weights were as follows: 1.22440, 1.22407.

The result of this experiment, together with the fact that a fine, white deposit was always found in the exit tubes on ignition, shows that tantalum oxide is certainly lost during ignition and also that it occludes a part of

the nitric acid giving it up, if at all, only after long ignition. Ruff and Schiller¹ have shown that when tantalum oxide is ignited with sulfuric acid a part of the acid is held, even after repeated ignitions.

As a result of these experiments it was concluded that the ignition and weighing of tantalum oxide obtained from the chloride could not be used for work of the highest accuracy and, therefore, the method was abandoned.

Ratio : TaCl_5 : 5Ag.—In the beginning of the investigation of this ratio an attempt was made to hydrolyze the tantalum chloride and precipitate the hydrochloric acid formed, with silver in the presence of the tantalic acid. It was soon evident, however, that the silver was being used up by a continual displacement of the equilibrium. In one experiment to determine the nature of this reaction a sample of tantalum oxide was boiled with water and allowed to stand for several days, when the supernatant liquid, which still had a faint opalescence, was poured off and tested with silver nitrate. The opalescence was quite noticeably increased, a fact which indicated that it would be necessary to remove the tantalic acid before precipitating the chloride with silver.

The method which seemed most suitable for the separation of the tantalic acid was to hydrolyze the tantalum chloride as before and distill off the hydrochloric acid. With the idea in mind that it might be possible to obtain the chloride-oxide ratio and the chloride-silver ratio from the same sample of tantalum chloride the quartz reaction flask, Fig. 2, was designed. The apparatus first used for the hydrolysis was the same as that already described in the study of the ratio $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$. The tantalum chloride was hydrolyzed in the quartz flask and the hydrochloric acid drawn into a liter flask where all but the last traces were absorbed. In order to prevent the escape of any acid, a series of twelve small bulbs was attached to the large absorbing flask. These were arranged with a gentle slope so that the gas was forced to bubble through the liquid in each of the bulbs. A solution containing a little excess of the calculated amount of sodium hydroxide to react with the hydrochloric acid was placed in the absorbing train. As a final guard against loss of chloride a bulb was sealed to the end of the absorbing train in such a way that the liquid in it could be removed and tested for any hydrochloric acid that might escape absorption. The analysis was made in a three-liter Erlenmeyer flask, by precipitation with a weighed amount of silver dissolved in nitric acid. The nephelometer was used here and in all succeeding analyses with silver to obtain the final end point. Standard solutions of silver nitrate and sodium chloride were used for this purpose.

In Table I are the results obtained in the analyses that were carried to completion without the known loss of hydrochloric acid.

¹ *Z. anorg. Chem.*, **72**, 329 (1911).

TABLE I.

| Cl = 35.46. | | NaCl : Ag = 0.54185. | | Ag = 107.88. | |
|-------------|---------------------------------------|-----------------------|---|-------------------|--|
| No. | Wt. of TaCl ₅ , (vac.). | Wt. of Ag, (vac.). | 100 parts of TaCl ₅ equivalent to parts of Ag. | Atomic weight. | |
| 5..... | 11.66795 | 17.51344 | 66.622 | 182.06 | |
| 9..... | 7.61398 | 11.42585 | 66.638 | 182.14 | |
| 11..... | 4.09519 | 6.15647 | 66.518 | 181.50 | |
| 12..... | 8.09039 | 12.16628 | 66.498 | 181.40 | |

The poor agreement was thought to be due to the amount of manipulation necessary for the transfer of the solution from the rather extended absorption train, since in none of these did any hydrochloric acid reach the test bulb. To obviate this difficulty it was determined to carry out the whole process of hydrolyzing the tantalum chloride and distilling off the hydrochloric acid in a sealed apparatus under reduced pressure. In order to determine the possibility of completely hydrolyzing the tantalum chloride under these conditions the following experiment was carried out:

A weighed amount of pure sodium chloride was suspended in a glass weighing bottle above a sulfuric acid solution (1 : 1) in a 500 cc. distilling flask which was sealed by means of a glass tube to another flask, used as a receiver. In the receiver was placed the calculated amount of pure sodium hydroxide solution required to neutralize the hydrochloric acid formed. The neck of the reaction flask was then sealed off, the receiver connected with a good water pump and the whole apparatus evacuated, and then closed by sealing the capillary connection between the receiver and the pump. By tipping the apparatus slightly the bottle containing the sodium chloride was dropped into the acid solution. The hydrochloric acid formed was then distilled over into the receiving flask where it was absorbed in the alkali. One determination made in this way gave 0.54189 for the ratio NaCl : Ag, which agrees very well with the value obtained by Richards and Wells¹ (0.54185). In a second experiment two or three grams of tantalum oxide, free from chloride, were placed in the reaction flask with the sodium chloride and the analysis carried out as before. Repeated distillation, however, failed to remove all the hydrochloric acid, though it was finally evaporated to dryness twice after moistening with one or two cubic centimeters of sulfuric acid each time.

From this it was evident that the hydrochloric acid could not be completely removed from the tantalum oxide at the temperature of boiling sulfuric acid. Therefore, a second analysis of sodium chloride in the presence of tantalum oxide was made as before, with the exception that the residue, obtained by twice evaporating the mixture to a syrupy consistency with sulfuric acid, was transferred to a 500 cc. platinum dish by rinsing out the flask with as little water as possible. Enough hydrofluoric

¹ *Pub. Carnegie Inst. Wash.*, No. 28 (1905).

acid was then added to form a clear solution and the chloride determined by adding an excess of silver nitrate and comparing the opalescence to that of standard sodium chloride solution treated in the same manner. The value obtained for the ratio $\text{NaCl} : \text{Ag}$ was 0.54211. A great deal of difficulty was encountered in transferring the residue from the reaction flask because of the fact that it formed with the sulfuric acid a mass of gummy particles which clung so tightly to the walls of the flask that it was impossible to remove it completely. This undoubtedly would account for a considerable part of the variation from the accepted ratio but the result seemed to indicate that the principle involved in the method might be used.

Not yet satisfied, however, that the silver nitrate would not form an insoluble compound with the tantalum under these conditions a sample of tantalum oxide, free from chloride, was dissolved in hydrofluoric acid and silver nitrate was added. No opalescence appeared within twelve hours.

The results obtained from this series of experiments indicated that it would be possible to determine the chloride by precipitation with silver nitrate in the presence of the tantalum fluoride, if enough hydrofluoric acid was used, to hold the tantalum in solution. If too little hydrofluoric acid was used, however, the silver formed an insoluble compound, probably a tantalate. Platinum was the most satisfactory material in which to carry out this reaction. Accordingly, a platinum Erlenmeyer flask having a capacity of about one and three-fourths liters and fitted with a platinum stopper, together with a small platinum weighing bottle was obtained for this work.

The method of analysis was as follows: The weighed platinum bottle together with a bulb containing the purified tantalum chloride was placed in the dry-box and the transfer made as described above. The stopper, also of platinum, was carefully replaced in the bottle and the whole transferred to the balance and weighed. One of Ruprecht's best balances was used throughout the investigation and the weights were carefully standardized. All weighings were made by substitution, using a platinum crucible of approximately the same weight as the bottle for tare. Sufficient pure water to make an approximately fifth normal solution with the tantalum chloride and enough hydrofluoric acid to dissolve the tantalic acid were placed in the platinum flask and warmed to a temperature slightly above that of the surrounding atmosphere. The stoppered bottle was then dropped into the solution and the flask quickly closed. The warm solution soon caused an expansion of the air within the bottle sufficient to force the stopper out and allow the hydrolysis of the tantalum chloride to take place. The calculated amount of silver to precipitate the chloride was weighed out to within one or two milligrams, dissolved in nitric acid

(1 : 1) and the solution made up to about fifth normal. The silver nitrate solution was then poured slowly into the chloride solution while the latter was being gently agitated. After a complete transfer to the silver nitrate, the flask was shaken for some time to insure a thorough mixing and then allowed to stand until the next day, when a sample of the clear supernatant liquid was removed for a nephelometric test. The flask and contents were cooled with ice for several hours before removing the sample in order to reduce the solubility of the silver chloride. The transfer was made to platinum crucibles by means of a pipet coated with pure paraffin. Excess of silver nitrate was added to one and sodium chloride to the other, after which they were allowed to stand for about eight hours before the nephelometric readings were taken.

Considerable difficulty was encountered in obtaining nephelometric tubes that would be sufficiently transparent and yet resistant to the action of the hydrofluoric acid. The ordinary glass tubes were coated with pure paraffin, collodion, etc., but with little success. It was found that they either diffused the light or dialyzed too readily. Finally, however, tubes were constructed by cementing together the edges of strips of celluloid and closing the ends of the cylindrical tubes thus formed with carefully cleaned rubber stoppers over which a thin layer of paraffin was placed. These tubes were found to be very satisfactory.

Table II contains the results of three analyses carried out by this method.

TABLE II.

| | Cl = 35.46. | NaCl : Ag = 0.54185. | Ag = 107.88. | |
|--------------|-------------------------------------|--------------------------|---|-------------------|
| Preparation. | Wt. of TaCl ₅ (vac.). | Weight of Ag. (vac.). | 100 parts of TaCl ₅ equivalent to parts of Ag. | Atomic weight. |
| I..... | 3.53605 | 5.31834 | 66.488 | 181.34 |
| II..... | 2.99083 | 4.49851 | 66.485 | 181.32 |
| III..... | 6.21118 | 9.34345 | 66.476 | 181.27 |

Although the agreement here is much better than any previously obtained it did not seem to be as good as the method should produce. The only reason for this that presented itself was that there was something about the equilibrium of the reaction that was not understood. So a study of this was taken up as follows:

Standard solutions of sodium chloride and silver nitrate were prepared, and equivalent amounts of these were mixed and allowed to stand for three days when a portion of the clear liquid was tested in the nephelometer. No difference was detected. In a second determination in which the same solutions were used enough hydrofluoric acid was added to make a 4.4% solution. The nephelometer again showed exact equivalence, which indicated that hydrofluoric acid alone did not affect the equilibrium.

A sample of sodium chloride was then weighed out, dissolved and precipitated with a weighed amount of silver in the usual manner. On the

following day a portion of the clear liquid tested in the nephelometer showed a slight excess of chloride. The calculated amount of silver was added from the standard solution and allowed to stand until the following day when a nephelometric test showed exact equivalence. In this experiment 1.78135 g. of sodium chloride required 3.28748 g. of silver for precipitation which gave 0.54185 for the ratio NaCl : Ag. This is in exact agreement with the value obtained by Richards and Wells. A second determination was carried out in the same way, using 1.79253 g. of sodium chloride to which had been added 0.31 g. of tantalum oxide dissolved in enough hydrofluoric acid to make a 5.5% solution. After a thorough mixing, the whole was set aside till the next day when a nephelometric test was made. This showed a considerable excess of sodium chloride though exact equivalents had been added. This seemed to indicate that equilibrium had not yet been reached, so the solution was again shaken for some time and set aside for another day when a nephelometric test showed a greater excess of sodium chloride than before. The shaking was repeated and a nephelometric test made on the next day showed only a very slight excess, which entirely disappeared on the fourth day. A third determination was made in which the percentage of hydrofluoric was kept the same but the amount of tantalum oxide added was doubled. Nephelometric tests made on the third and fifth days after precipitation showed exact equivalence. Other determinations were made in which the percentage of hydrofluoric acid was decreased but without obtaining satisfactory results.

These experiments indicated that it would be possible to determine accurately the amount of chloride present in a hydrofluoric acid solution containing a sufficient amount of the latter, but that a longer time would be required for the equilibrium to be reached than in the case of sodium chloride. With this in mind five analyses of tantalum chloride prepared by the method already described, but further treated as described below, were carried out and the results are given in Table III.

TABLE III.

| | | | | |
|----------------------|--|--------------------------|--|-------------------|
| | Cl = 35.46. | NaCl : Ag = 0.54185. | Ag = 107.88. | |
| | | | 100 parts of | |
| Preparation. | Weight of TaCl ₅ (vac.). | Weight of Ag. (vac.). | TaCl ₅ equivalent to parts Ag. | Atomic weight. |
| A..... | 4.03892 | 6.07417 | 66.493 | 181.36 |
| B ₁ | 3.32164 | 5.00133 | 66.417 | 180.96 |
| B ₂ | 2.68304 | 4.04002 | 66.412 | 180.93 |
| B _a | 3.01453 | 4.53953 | 66.406 | 180.90 |
| B _b | 3.95846 | 5.95931 | 66.425 | 181.00 |

In preparation A the chlorine was replaced with dry air and the tantalum chloride was redistilled under atmospheric pressure. Preparation B was treated in the same manner except that it was redistilled under slightly reduced pressure. In preparation B five samples were obtained of which the third and fourth (B₃ and B₄) were analyzed without further treatment.

Samples 1 and 2, however, were subjected to a further distillation under atmospheric pressure and formed preparation B₆. Sample 5 was treated in as nearly the same manner as was possible at different times and formed preparation B₆.

The results obtained in this series seem to indicate that tantalum chloride either occludes some chlorine which may be removed only with the greatest care or that it is partially decomposed by distillation in dry air. The former would tend to give a low value for the atomic weight while the latter would undoubtedly give a value too high.

Summary.

During the present study of the ratios $2\text{TaCl}_5 : \text{Ta}_2\text{O}_5$ and $\text{TaCl}_5 : 5\text{Ag}$, the following observations were made:

1. Tantalum oxide, prepared from the chloride, not only occludes the nitric acid but is lost on ignition.
2. Silver forms with tantalic acid an insoluble compound, probably a tantalate.
3. Hydrochloric acid cannot be removed completely from tantalic acid by boiling with sulfuric acid either under atmospheric or reduced pressure.
4. Silver can be used to determine hydrochloric acid in the presence of tantalum fluoride if the precipitation is carried out in an approximately 5.5% solution of hydrofluoric acid. Three to four days, however, are necessary for equilibrium to become established.
5. Tantalum chloride, purified by replacing the chlorine atmosphere with dry air and by distilling either under atmospheric or reduced pressure, apparently varies slightly in composition.

In conclusion it may be pointed out that there is now available for the first time a method of analysis sufficiently accurate to detect slight differences in the composition of tantalum chloride. It now remains to make a careful study of the preparation of the chloride with regard to the definiteness of its composition. This problem is now under investigation and as soon as a satisfactory solution is obtained a final series of determinations will be published. It may be added that the possible value of this method of analysis for the determination of the atomic weights of other elements will be investigated.

URBANA, ILL.

[CONTRIBUTION FROM THE UNITED STATES GEOLOGICAL SURVEY.]

SOLUBILITY OF MIXTURES OF SODIUM AND POTASSIUM CHLORIDES IN SOLUTIONS OF HYDROCHLORIC ACID.¹

By W. B. HICKS.

Received February 3, 1915.

Some experiments conducted by Dr. R. C. Wells of the Geological Survey on the brines from Great Salt Lake indicated that potassium

¹ Published by permission of the Director of the U. S. Geological Survey.

chloride is more soluble in hydrochloric acid solutions than is sodium chloride, and led to the suggestion that the constant boiling point acid might serve as a useful reagent in the commercial separation and purification of these two salts. In order to investigate the possibilities in this direction, it was decided to determine the solubilities of mixtures of sodium and potassium chlorides in several different concentrations of hydrochloric acid, including that of the constant boiling point acid. For this purpose acid solutions of approximately 8, 17, 20 and 32% were prepared, the exact strength being determined afterwards on the saturated solution of the mixed salts by titration with standard sodium hydroxide solution. While the results, as was to be expected, soon showed that the solubility of these salts in strong acid is too small to admit of the reagent being used commercially under ordinary circumstances, the experiments were not without interest, in that an increase in the potassium-sodium ratio went hand in hand with that of the concentration of the acid.

The apparatus used in all the solubility determinations was in principle similar to that described by C. M. van Deventer¹ and later used by H. Goldschmidt² and others, and is accurately represented in the following diagram.

The glass cylinder *a* is 20 cm. long and 3.8 cm. in diameter and carries two one-hole rubber stoppers *c* and *d*. The tube *e* is used for stirring and carries the pulley *f* by which it is rotated. The enlargement at *g* contains two small holes, *h* and *i*, for the purpose of increasing the efficiency of the stirrer. The hollow wooden cylinder *j* is held in place by the rubber stopper *c*, supports the pulley *f*, and serves as a bearing in which the stirrer *e* rotates. The glass rod *k* carries the rubber stopper *l* which closes the filtering tube *m*. The platinum cone *n* supports the asbestos filter *o*. The syphon *p* is sealed to *m*, and extends through the rubber stopper *q* into the 50 cc. flask *r*. The small tube *s* serves as an outlet for *r*.

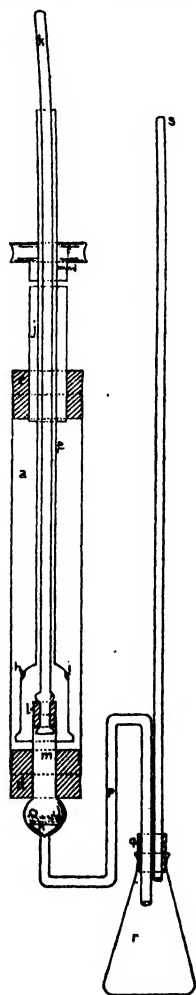


Fig. 1.

In conducting the experiments about 15 g. of pure potassium chloride and an equal quantity of sodium chloride were placed in the glass container *a* of the apparatus described above, and then 40 cc. of hydrochloric acid

¹ *Z. physik. Chem.*, **5**, 559 (1890).

² *Ibid.*, **17**, 153 (1895).

approximately of the strength desired were added. The whole apparatus was placed in an electrically controlled thermostat to such a depth that the water reached to within about one inch of the top of the container *a*, and was clamped in place. The thermostat fluctuated less than 0.05° from 25° . The mixture was stirred energetically for 4 hours, when the solution was considered to be saturated, preliminary experiments having shown that ordinarily equilibrium is attained in a much shorter time under such conditions. After allowing the undissolved salts to settle, the rubber stopper was removed from the filter tube by means of the glass rod *k*, and the saturated solution filtered at the thermostat temperature through the asbestos mat into the weighed flask *r*. Suction was applied at *s* to hasten the filtering operation. The whole apparatus was then removed from the thermostat, the flask washed with water at 25° , dried, removed from the apparatus and weighed.

The weighed solution, amounting to about 30 g., was made to definite volume and aliquots taken for analysis. In most cases the determinations were carried out in duplicate. The acidity was determined by titration with standard sodium hydroxide solution, using methyl orange as indicator. The potassium was determined by precipitating as potassium chloroplatinate and weighing the reduced platinum.¹ The total dissolved salts were estimated by evaporating a definite mount of the solution in platinum and weighing the residue after gentle ignition and cooling in a desiccator. The values for sodium were obtained by difference.

TABLE I.—SOLUBILITY OF MIXTURES OF SODIUM AND POTASSIUM CHLORIDES IN HYDROCHLORIC ACID SOLUTIONS AT 25° .

| No. | % HCl. | % NaCl. | % KCl. | % NaCl + KCl. | % Na. | % K. | Ratio K/Na. |
|--------|--------|---------|--------|------------------|-------|------|----------------|
| 1..... | 0 | 19.95 | 10.90 | 30.85 | 7.85 | 5.72 | 0.73 |
| 2..... | 8.61 | 10.65 | 7.58 | 18.23 | 4.19 | 3.98 | 0.95 |
| 3..... | 17.16 | 3.56 | 3.80 | 7.36 | 1.40 | 1.99 | 1.42 |
| 4..... | 20.65 | 2.03 | 2.86 | 4.89 | 0.80 | 1.50 | 1.87 |
| 5..... | 32.78 | 0.18 | 1.27 | 1.45 | 0.07 | 0.67 | 9.57 |

The results of the solubility determinations are given in Table I. In order to make the data more complete, the values of Precht and Wittjen² for the solubility of mixtures of sodium and potassium chlorides in pure water have been included, the figures for 25° having been obtained by interpolation. The results have also been plotted showing graphically the changes in solubility of these salts with variations in the concentration of the acid. This diagram is given in Fig. 2.

The rapid depression in the solubility of sodium and potassium chlorides with the increase in the concentration of the acid is very striking and is

¹ Hicks, W. B., "A rapid modified chloroplatinate method for the estimation of potassium," *J. Ind. Eng. Chem.*, **5**, 650 (1913).

² *Ber.*, **14**, 1667 (1881).

of the same order as that shown by the individual salts in solutions¹ of hydrochloric acid.¹ It is much more pronounced for sodium chloride than for the potassium salt, so that the curves representing these two solubilities intersect at a point corresponding to 16.2% of hydrochloric acid. Here the solubilities of the two salts are equal, amounting to 4.4%. As the acid solution becomes still more concentrated the saturated mixture con-

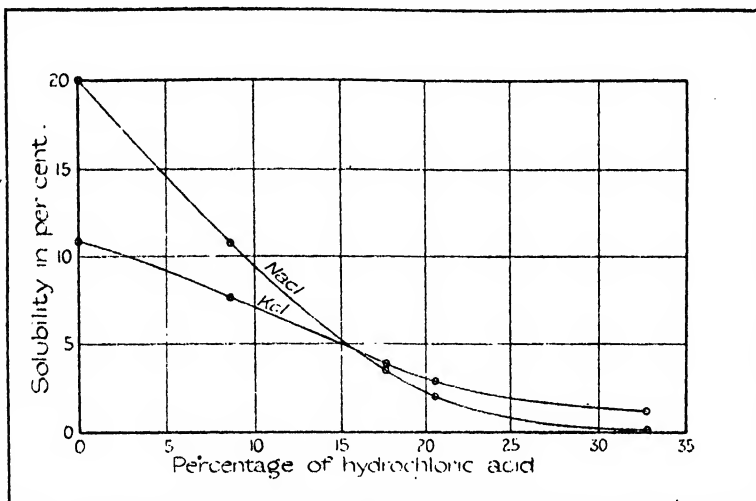


Fig. 2.

tains an increasingly larger proportion of potassium than of sodium chloride. However, in such strong acid solutions the solubility of both salts is very small, amounting to only 2.9% of potassium chloride and 2.2% of sodium chloride in the constant boiling point (20.3%) acid. Apparently this precludes the consideration of hydrochloric acid as a reagent in the commercial separation of the two salts in question.

WASHINGTON, D. C.

AMMONOBASIC ALUMINIUM IODIDES.

BY EDWARD C. FRANKLIN.

Received January 15, 1915.

Introduction.

Some years ago the observation was made that very considerable quantities of potassium amide may be added to liquid ammonia solutions of aluminium iodide without causing the formation of a permanent precipitate. With further additions of the alkaline amide a precipitate is formed which then dissolves again in an excess of potassium amide.²

In the light of the many demonstrated analogies between the reactions

¹ Engel, *Ann. de Chim. Phys.*, [6] 13, 374 (1888).

² THIS JOURNAL, 27, 849 (1905).

which take place in the two solvents ammonia and water the probable explanation of these observations is, first that the solution to which a limited amount of potassium amide has been added contains a soluble ammonobasic iodide of aluminium; second, that the precipitate is either an insoluble ammonobasic iodide or aluminium amide and, third, that the solution of the precipitate in an excess of potassium amide results in the formation of an ammonoaluminate of potassium.

It was for the purpose of attempting the isolation of a soluble ammonobasic aluminium iodide that the present investigation was undertaken. At the same time it was hoped that the experience in the manipulation of liquid ammonia solutions gained in the interim might enable the experimenter to isolate an ammonoaluminate of potassium and to show the insoluble precipitate studied several years ago¹ to be an ammonobasic salt of definite composition. A beautifully crystalline ammonobasic iodide of aluminium has been isolated and the existence of an insoluble ammonobasic salt is shown to be probable, but the extreme solubility of the product of the action of excess of potassium amide on aluminium iodide has so far rendered ineffectual all attempts to isolate an ammonoaluminate of potassium.

Preparation of Aluminium Iodide.—For the purposes of this investigation a quantity of aluminium iodide was synthesized by the interaction of aluminium turnings and iodine and prepared for use by distillation in vacuum into long glass tubes after the manner described by Fitzgerald.² The salt distills over as a clear, colorless liquid which soon solidifies to a crystalline solid. As a check on the purity of the salt an analysis was made, with the result that it was found to contain 6.6% aluminium and 93.1% iodine. Theoretically aluminium iodide should contain 6.6% aluminium and 93.4% iodine.

Ammonated Aluminium Iodide, $AlI_3 \cdot 6NH_3$ and $AlI_3 \cdot 20NH_3$.—When ammonia gas is brought into contact with aluminium iodide vigorous absorption takes place which, unless the action be restrained, produces sufficient elevation of the temperature to volatilize some of the material. When the salt is introduced into the reaction apparatus contained in sections of glass tubing cut from the containers described by Fitzgerald¹ then the action of the solvent on the salt is accompanied by more or less active boiling of the liquid in immediate contact with the salt, but the large mass of liquid and the small surface of contact between the liquid and the salt effectively prevents too great a rise in temperature. Aluminium iodide is extremely soluble in liquid ammonia. At -33° the very concentrated solution solidifies to a mass of crystals containing about 20 molecules of ammonia of crystallization. At 8° to 13° these

¹ *Loc. cit.*

² THIS JOURNAL, 29, 1694 (1907).

crystals melt, but before fusion is complete there begins the separation of crystals containing less ammonia of crystallization, presumably a compound of the composition represented by the formula $\text{AlI}_2.6\text{NH}_3$. On further elevation of the temperature the quantity of this latter salt separating from the solution greatly increases. On cooling, these crystals again go into solution but usually before they are completely dissolved the whole liquid solidifies to a mass of the more highly ammonated salt. One obviously here observes a transition point similar to the many familiar examples taking place in water solutions.

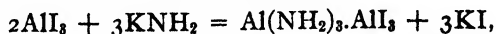
The composition of one ammonated salt is fixed by the following analytical data. The composition of other more highly ammonated salts remains uncertain though the existence of a compound of the formula $\text{AlI}_3.20\text{NH}_3$ seems to be established.

A portion of the ammonated salt dried in vacuum at 100° to 190° weighed 1.0730 g., one-fourth of which gave 0.0289 g. Al_2O_3 . Another fourth gave 0.3703 g. AgI and a third fourth gave 0.0531 g. N. At -33° this specimen of salt retained in one experiment 0.4763 g. NH_3 , in another 0.5065 g. NH_3 .

| | Calculated for $\text{AlI}_2.6\text{NH}_3$. | Found. |
|---------|---|--------|
| Al..... | 5.3 | 5.7 |
| I..... | 74.7 | 74.6 |
| N..... | 20.0 | 19.8 |

Calculated for 14NH_3 , 46.7; found, 44.4 and 47.2.

Soluble Ammonobasic Aluminium Iodide, $\text{Al}(\text{NH}_2)_3.\text{AlI}_2.6\text{NH}_3$.—Pure aluminium iodide dissolves in liquid ammonia to a perfectly clear, colorless solution.¹ When potassium amide is added to such a solution a white, amorphous precipitate is formed which redissolves on mixing the contents of the reaction tube. This operation is continued until a very considerable amount of potassium amide has been added, but is stopped short of the formation of a permanent precipitate. The work described below shows that there is in solution a soluble ammonobasic salt formed in accordance with the equation



and that the permanent precipitate formed by further additions of potassium amide to the solution of aluminium iodide is another ammonobasic salt containing much less iodine.

In order to isolate the soluble ammonobasic salt, the solution prepared as described above its evaporated until a satisfactory crop of crystals is deposited but not so far as to bring about the separation of any crystals of potassium iodide from the solution. The mother liquor is then poured into the second arm of the reaction tube and sufficient solvent is distilled

¹ The suggestion made in an earlier paper (THIS JOURNAL, 27, 849 (1905)) that an insoluble residue left on dissolving aluminium iodide in liquid ammonia was probably an ammonobasic salt is, therefore, erroneous.

from the mother liquor back upon the crystals to bring them into solution. Such portions of the solvent are again evaporated away as will result in a good crop of crystals when the mother liquor is again drained from the crystals. This operation is repeated until, in the judgment of the operator, the compound is pure or until the crop of crystals becomes so small as to render further recrystallization inadvisable. The leg containing the salt is then sealed off from the reaction tube and, after evaporating the excess of ammonia, is weighed preparatory to analysis, for which latter purpose the salt is first hydrolyzed by water and then dissolved in dilute sulfuric acid. The aluminium, iodine and ammonia in the solution thus obtained are determined by the well-known methods; aluminium as the oxide, iodine as silver iodide and ammonia by distillation with sodium hydroxide and titration after the usual manner. Following are recorded the experimental results obtained:

Preparation I.—The salt prepared as described above was recrystallized twice and dried in vacuum at 20°. The specimen weighed 0.5007 g., of which one-fourth gave 0.0222 g. Al_2O_3 . Another fourth gave 0.0287 g. N and another fourth gave 0.1416 g. AgI.

Preparation II.—In this experiment 7.5 g. of aluminium iodide were used and the first crop of crystals obtained was recrystallized three times. Dried in vacuum at 100° the specimen weighed 1.5820 g. One-fourth gave 0.0692 g. Al_2O_3 , another fourth gave 0.4757 g. AgI, one-tenth gave 0.0346 g. N and another tenth gave 0.0343 g. N.

Preparation III.—Ten grams of aluminium iodide were used and the basic salt was recrystallized three times. Dried in vacuum at 130° the specimen weighed 1.7605 g. One-fourth of the specimen gave 0.0783 g. Al_2O_3 , another fourth gave 0.5273 g. AgI and one-tenth gave 0.0365 g. N.

Preparation IV.—This specimen was obtained from the mother liquor from Preparation III. It was recrystallized three times and dried in vacuum at 200°. It weighed 0.7964 g. One-fourth gave 0.0356 g. Al_2O_3 , another fourth gave 0.0425 g. N and one-half gave 0.4802 g. AgI.

Preparation V.—This specimen was made from 4.4 g. of aluminium iodide and was recrystallized four times preparatory to analysis. After sealing apart the two legs of the reaction tube the solution of the salt was found to be milky from the presence of some impurity, presumably a small quantity of the insoluble ammonobasic salt described below. Dried at 165° in vacuum the specimen weighed 1.7343 g., one-fourth of which gave 0.0773 g. Al_2O_3 . Another fourth gave 0.5280 g. AgI and one-tenth gave 0.0370 g. N.

| | Calculated for $\text{Al}(\text{NH}_2)_2.\text{AlI}_2.6\text{NH}_3$. | Found. | | | | |
|---------|--|--------|------|------|------|------|
| | | I. | II. | III. | IV. | V. |
| Al..... | 9.2 | 9.3 | 9.2 | 9.4 | 9.5 | 9.4 |
| I..... | 65.1 | 61.2 | 65.0 | 64.8 | 65.3 | 65.8 |
| N..... | 21.6 | 22.2 | 21.6 | 20.7 | 21.4 | 21.3 |

A soluble ammonobasic iodide of aluminium therefore results from the action of potassium amide on aluminium iodide in liquid ammonia solution in accordance with the equation given above. It is readily soluble in liquid ammonia, the solubility greatly increasing as the temperature is lowered. At laboratory temperatures the salt separates in beautifully

formed crystals containing six molecules of ammonia which are not given off even at a temperature of 200° . As the temperature of the solution in equilibrium with the hexammonate crystals is lowered, the crystals dissolve and at the still lower temperature furnished by a bath of liquid ammonia the solution solidifies to a mass of needle-like crystals of the composition represented by the formula $\text{Al}(\text{NH}_2)_3.\text{AlI}_3.18\text{NH}_3$.¹ This salt melts in the neighborhood of zero, more or less of the hexammonate separating from the solution at the same time. Obviously one has to do with a transition point similar to that shown by aluminium iodide described above.

Insoluble Ammonobasic Aluminium Iodide, $\text{Al}(\text{NH}_2)_3.\text{Al}(\text{NH}_2)_2\text{I.NH}_3$ and $\text{Al}(\text{NH}_2)_3.\text{Al}(\text{NH})\text{I}$.—When potassium amide is added to a solution of the soluble salt described above an amorphous, bulky precipitate of an insoluble basic salt is formed which settles very sluggishly and never to small bulk. The process of washing is therefore exceedingly tedious and time consuming, for which reason the preparation of a second specimen has not been attempted. The precipitate was washed 18 times by decantation, but since only about one-third of the liquid could be removed at each washing there is no certainty that the precipitate was thoroughly washed. The product was prepared for analysis in a manner similar to that described above for the soluble salt.

The specimen, dried in vacuum at 20° , weighed 0.4570 g. Dried at 160° it weighed 0.4135 g. One-fourth of the specimen dried at 160° gave 0.0414 g. Al_2O_3 , another fourth gave 0.0224 g. N and a third fourth gave 0.1043 g. AgI.

From the data thus recorded the following results have been calculated:

| | Calculated for $\text{Al}(\text{NH}_2)_3.\text{AlNH}_2\text{I}$ | Found. |
|---------|--|--------|
| Al..... | 22.2 | 21.2 |
| N..... | 22.9 | 21.6 |
| I..... | 52.0 | 54.4 |
| | Calculated for $\text{Al}(\text{NH}_2)_3.\text{Al}(\text{NH}_2)_2\text{I.NH}_3$ | Found. |
| Al..... | 19.4 | 18.1 |
| N..... | 30.2 | 30.8 |
| I..... | 45.6 | 46.2 |

It seems probable, therefore, that an ammonobasic iodide of aluminium of the composition represented by the formula $\text{Al}(\text{NH}_2)_3.\text{Al}(\text{NH}_2)_2\text{I.NH}_3$ is formed by the action of potassium amide on a solution of aluminium

¹ As is the case with the more highly ammonated iodide of aluminium the amount of ammonia contained in this compound above six molecules appears to be difficult to fix. Four determinations of the amount of ammonia retained by the hexammonate at -33° gave 36.0, 38.3, 40.6 and 38.8%. Twelve molecules require 34.9%, 14 molecules requires 40.7%. Because of the time-consuming nature of the operations involved in establishing equilibrium between an ammonated salt and ammonia in the case of ammonated salts showing a considerable vapor tension at low temperatures further attempts to fix the composition of this compound were abandoned.

iodide¹ and that the compound thus formed loses two molecules of ammonia on being heated to 160°. In view of the amorphous character of the precipitate, however, the existence of a definite compound of the composition given cannot be certain. At all events it is an insoluble ammonobasic product.

Summary.—A soluble ammonobasic iodide of aluminium is formed in accordance with the reaction represented by the equation $2\text{AlI}_3 + 3\text{KNH}_2 = \text{Al}(\text{NH}_2)_3.\text{AlI}_3 + 3\text{KI}$, when potassium amide in limited amount is added to a liquid ammonia solution of aluminium iodide. At ordinary temperature the salt separates from solution with six molecules of ammonia of crystallization as represented by the formula $\text{Al}(\text{NH}_2)_3.\text{AlI}_3.6\text{NH}_3$, at low temperatures a highly ammonated salt containing from 18 to 20 molecules of ammonia separates from the solution.

An insoluble ammonobasic iodide of aluminium, the composition of which is represented by the formula $\text{Al}(\text{NH}_2)_3.\text{Al}(\text{NH}_2)_2\text{I}.\text{NH}_3$ is precipitated when potassium amide is added to a solution of the above soluble basic salt. When heated this compound loses two molecules of ammonia to form a product to which the formula $\text{Al}(\text{NH}_2)_3.\text{AlNHI}$ has been given.

STANFORD UNIVERSITY, CALIFORNIA.

POTASSIUM AMMONOARGENTATE.

By EDWARD C. FRANKLIN.

Received January 15, 1915.

Some years ago while studying the action of potassium amide on liquid ammonia solutions of silver salts, the observation was made that silver amide dissolves readily in excess of potassium amide solution.² Since this is a behavior which recalls the similar action of water solutions of potassium hydroxide on certain metallic hydroxides it was surmised that the observed action of potassium amide solution on silver amide probably results in the formation of an ammonoargentate of potassium.

It was for the purpose of attempting the isolation of such a compound that this investigation was undertaken.

When, in one of the two-legged reaction tubes which have been elsewhere described,³ a liquid ammonia solution of potassium amide is run into a similar solution of a silver salt a precipitate of silver amide is formed which, as the addition of potassium amide is continued, increases in amount until all the silver is precipitated. With further addition of the precipitant the precipitate dissolves to a clear, colorless solution. When, after a proper adjustment of the concentration, the solution thus obtained is cooled in a bath of liquid ammonia a crop of beautiful crystals separates from the

¹ Cf. analytical results given in *THIS JOURNAL*, 27, 849 (1905).

² *THIS JOURNAL*, 27, 835 (1905).

³ *Ibid.*, loc. cit.

solution. The salt is purified by recrystallizing several times from solvent distilled over from the second arm of the reaction tube. After separating the two legs of the reaction tube containing, respectively, the mother liquor and the solution of the pure salt, the excess of ammonia is removed from the latter and the pure, dry salt, together with its container, is weighed. In order to hydrolyze the specimen and get the hydrolytic products into aqueous solution preparatory to analysis, the dried salt is allowed to lie over night in contact with water vapor. The hydrolytic products were then treated successively with liquid water and dilute sulfuric acid. It was expected that the salt, which has been shown to have the composition represented by the formula $\text{AgNHK} \cdot \text{NH}_3$, would hydrolyze in accordance with the equation $2\text{AgNHK} + 3\text{H}_2\text{O} = \text{Ag}_2\text{O} + 2\text{KOH} + 2\text{NH}_3$. Contrary, however, to expectations it was found that considerable quantities of metallic silver and nitrogen gas are always liberated during this treatment of the compound. Furthermore, when the salt was prepared directly from iodide of silver in the manner described above, small quantities of the latter salt were always found mixed with the metallic silver. This contamination was not a portion of the original iodide of silver used in the experiment, but resulted from the action of potassium iodide, which had not completely removed from the salt by the process of purification to which it was submitted, on the silver sulfate formed by the action of the dilute sulfuric acid on the products of hydrolysis. The metallic silver was recovered from the mixture of silver and silver iodide by dissolving in dilute nitric acid and precipitating it as silver chloride. The silver chloride thus obtained is marked (a) in the analytical data below. The silver iodide, which was filtered off, washed, weighed and is marked (b) below, gives a measure of the amount of potassium iodide with which the specimen was contaminated. The silver contained in the sulfuric acid solution was precipitated as the chloride and is given under (c) in the analytical data. The total nitrogen was made up of two parts, that present in the sulfuric acid solution as ammonium sulfate and that set free during the hydrolysis of the ammono salt. The free nitrogen and metallic silver were found to be formed in equivalent quantities.

Preparation I.—In this experiment somewhat more than two equivalents of potassium amide were added to a solution of 2.35 g. of silver iodide in liquid ammonia and the resulting solution, after proper concentration, was cooled to -40° . The crop of beautiful crystals which separated from the solution was dissolved and recrystallized once for analysis.

The specimen dried in vacuum at 20° weighed 0.8880 g. The specimen contained 0.4636 g. Ag, calculated from (a) 0.4506 g. AgCl, (b) 0.1268 g. AgI and (c) 0.0525 g. AgCl from three-fifths of the sulfuric acid solution. The other two-fifths of this solution gave 0.0429 g. N. The free nitrogen collected amounted to 0.0142 g. One-fifth of the filtrate from (c) gave 0.0557 g. K_2SO_4 .

Preparation II.—The same quantities of silver iodide and potassium amide were used as in the preceding experiment.

The salt, recrystallized four times and dried in vacuum at 20° , weighed 0.5479 g. The specimen contained a total of 0.3211 g. Ag, calculated from (a) 0.3755 g. AgCl, (b) 0.0078 g. AgI and (c) 0.0465 g. AgCl from the whole of the sulfuric acid solution, and a total of 0.0867 g. N, calculated from the nitrogen equivalent of metallic silver (a) and 0.0186 g. N obtained from one-fourth of the filtrate from AgCl (c). Another fourth of this filtrate gave 0.0688 g. K_2SO_4 .

Preparation III.—In this experiment slightly more than three equivalents of potassium amide were added to a solution of 2.5 g. of silver iodide with the object in view of ascertaining whether possibly a salt containing two atoms of potassium may be obtained.

The specimen, which was recrystallized four times, weighed 0.4603 g. when dried in vacuum at 20° . It was found to contain a total of 0.2732 g. Ag, calculated from (a) 0.3075 g. AgCl, (b) 0.0065 g. AgI and (c) 0.0386 g. AgCl from three-fourths of the sulfuric acid solution. One-fourth of this solution gave 0.0158 g. N, which, together with the nitrogen equivalent of (a), gives a total of 0.0732 g. N. One-half of the filtrate from AgCl (c) gave 0.0826 g. K_2SO_4 .

Preparation IV.—Finding the silver persistently low in the above preparations, as the result of contamination with potassium iodide, it was determined to prepare pure silver amide and dissolve this in a solution of potassium amide with the expectation that a pure specimen of potassium ammonioargentate would result. Accordingly a three-legged reaction tube was prepared and into one leg was introduced 1 g. of silver nitrate and into each of the other two one equivalent of metallic potassium together with a minute quantity of platinum black.¹ Ammonia was distilled into the apparatus and after all the potassium had been converted into potassium amide the solvent from one of the legs containing potassium amide was evaporated away, leaving the ammonio base clinging to the walls and bottom of the tube. This potassium amide was reserved for dissolving the pure silver amide. The preparation and purification of silver amide was then carried on in the other two legs of the reaction tube after the manner previously described.² After thoroughly washing the silver amide, liquid ammonia was distilled from the washings and distributed between the two legs containing the precipitate and the reserve potassium amide, respectively. The leg containing the washings was then sealed off leaving a two-legged tube in which the operations of dissolving the silver amide and purifying the resulting salt were carried on in the usual manner. The crop of crystals obtained was recrystallized once preparatory to analysis.

Dried in vacuum at 100° the specimen weighed 0.4852 g. The metallic silver formed during the hydrolysis of the salt was dissolved in dilute nitric acid and added to the sulfuric acid solution. From the combined solutions 0.3877 g. AgCl

¹ Platinum black accelerates the reaction between the ammonia and potassium.

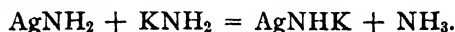
² *Loc. cit.*

was obtained. One-half of the filtrate from the silver chloride gave 0.0310 g. N, which, together with 12.7 cc. N measured over water at 20° and 760 mm., gives a total of 0.0765 g. N. The other half of the filtrate gave 0.1169 g. K_2SO_4 .

The following results have been calculated from the above data:

| | Calculated for AgNHK.NH ₃ . | Found. | | | |
|---------|---|--------|------|------|------|
| | | I. | II. | III. | IV. |
| Ag..... | 60.3 | 52.3 | 58.6 | 59.3 | 60.2 |
| N..... | 15.6 | 13.7 | 15.8 | 15.9 | 15.7 |
| K..... | 21.8 | 23.4 | 22.5 | 21.4 | 21.6 |
| I..... | 0.0 | 7.7 | 0.9 | 0.7 | |

A compound of the composition represented by the formula $AgNHK.NH_3$ or $AgNH_2.KNH_2$ is therefore formed by the action of a solution of potassium amide on the amide of silver in accordance with a reaction represented by the equation



The salt separates from concentrated solutions in the form of beautiful crystals which are unaffected at a temperature of 100°. It is gradually discolored and decomposed by contact with the air. When heated over the open flame it decomposes vigorously but without explosive violence. In contact with water it decomposes but does not explode. This behavior is in marked contrast with that of silver amide which, it will be remembered, explodes with great violence on the slightest provocation, frequently without any assignable cause whatever. Liquid ammonia solutions of acids decompose potassium ammonoargentate, precipitating first silver amide which dissolves on further addition of the acid to form a silver salt of the acid used.

Summary.—It is shown in this paper that silver amide dissolves in a liquid ammonia solution of the ammono base, potassium amide, to form potassium ammonoargentate, an ammono salt of the composition represented by the formula $AgNHK.NH_3$ or $AgNH_2.KNH_2$.

STANFORD UNIVERSITY, CALIFORNIA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI.]
**INTERPRETATIONS OF SOME STEREOCHEMICAL PROBLEMS
 IN TERMS OF THE ELECTRONIC CONCEPTION OF
 POSITIVE AND NEGATIVE VALENCES.¹**

**PART III: A CONTINUATION OF THE INTERPRETATION OF THE BROWN
 AND GIBSON RULE. PART IV: THE SIMULTANEOUS FORMATION
 OF ORTHO-, META- AND PARA-SUBSTITUTED DERIVATIVES
 OF BENZENE. PART V: A REPLY TO A. F. HOLLEMAN.**

By HARRY SHIPLEY FRY.
 Received January 21, 1915.

Introduction.

In the first paper (I)² of this series, the electronic conception of positive

¹ Read before the Cincinnati Section, Am. Chem. Soc., Dec. 9, 1914.

² Fry, *THIS JOURNAL*, 36, 248 and 262 (1914).

and negative valences and the electronic formula for benzene were employed to interpret the anomalous behavior of many of the derivatives of benzene. In the second paper (II)¹ halogen substitution in the benzene nucleus and in the side-chain was considered from the same points of view. In each of these papers the theoretical deductions presented and applied were shown to be in accord with the experimental facts under consideration.

The present papers (III, IV, V) of the series are presented under one cover because they relate in general to the interpretation of the problems encountered in the simultaneous formation of ortho-, meta-, and para-substituted derivatives of benzene, and likewise to the simultaneous formation of the more complicated polysubstituted derivatives of benzene.

In Part III (A Continuation of the Interpretation of the Brown and Gibson Rule) a further analysis of this rule, based upon experimental facts, leads to deductions which are employed throughout the subsequent papers.

Part IV presents (1) an explanation of the simultaneous formation of ortho-, meta-, and para-substituted derivatives of benzene based upon the conception of *electronic isomerism* and the existence of *electromers in dynamic equilibrium*, i. e., *electronic tautomerism*. (2) A mechanism of these changes is described. (3) Holleman's proposed mechanism of, and hypotheses relating to, substitution are interpreted in terms of the electronic conception of positive and negative valences. (4) It is shown that there is a direct correlation of the author's electronic formula for benzene and rule for substitution with Holleman's hypotheses.

Part V presents a direct reply to each of the objections which Holleman has just recently published² against the author's electronic formula for benzene (abbreviated formula, Fig. 1) and general rule of substitution. This rule maintains that when substituents are of the same sign or polarity they occupy positions which are meta to each other, but if two substituents are of opposite sign or polarity they will occupy positions either ortho or para to each other. This follows from the fact that the electronic formula of benzene is the only formula which presents a structural basis and an electronic interpretation for the relations between the ortho and para positions and substituents in contradistinction to the meta positions and substituents.

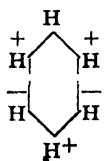


Fig. 1.

III. A CONTINUATION OF THE INTERPRETATION OF THE BROWN AND GIBSON RULE.³

(A) The Brown and Gibson Rule.⁴

The numerous instances in which certain monosubstituted derivatives

¹ THIS JOURNAL, 36, 1035 (1914).

² Holleman, *Ibid.*, 36, 2495 (1914).

³ See Fry, *Z. physik. Chem.*, 76, 385 and 398 (1911) for a detailed description of this rule and the derivation of the electronic formulas of benzene.

⁴ *J. Chem. Soc.*, 61, 366 (1892).

of benzene yield chiefly ortho and para disubstituted compounds, while other mono derivatives yield chiefly meta disubstituted products, have led to the formulation of the Brown and Gibson rule, the essential features of which must be briefly outlined. In the following abridged table,

| A. | B. | C. | D. | E. |
|----------------|------------|--------------|----------------|------------|
| C_6H_5X | X | H.X | HO.X | ... |
| C_6H_5Cl | Cl | H.Cl* | HO.Cl | <i>o-p</i> |
| $C_6H_5CH_3$ | CH_3 | H. CH_3 * | HO. CH_3 | <i>o-p</i> |
| $C_6H_5NH_2$ | NH_2 | H. NH_2 * | HO. NH_2 | <i>o-p</i> |
| C_6H_5OH | OH | H.OH* | HO.OH | <i>o-p</i> |
| $C_6H_5NO_2$ | NO_2 | H. NO_2 | HO. NO_2 * | <i>m</i> |
| C_6H_5COH | COH | H.CO H | HO.CO H * | <i>m</i> |
| C_6H_5COOH | COOH | H.CO OH | HO.CO OH * | <i>m</i> |
| $C_6H_5SO_2OH$ | SO $_2$ OH | H.SO $_2$ OH | HO.SO $_2$ OH* | <i>m</i> |

Column A contains the formulas of a few monosubstituted derivatives; Column B, a few of the common substituents; Column C, the hydrogen compounds of these substituents; Column D, the hydroxyl compounds of the same substituents; Column E, the letters (*o-p*) or (*m*), according as the mono-derivatives give chiefly a mixture of ortho- and para-derivatives, or chiefly meta-derivatives. Brown and Gibson maintained that those substances marked with an asterisk in Column C "are not capable, by direct oxidation in one step, of being converted into the corresponding hydroxyl compound" in Column D. On the other hand, those substances asterisked in Column D can be formed by direct oxidation from the corresponding hydrogen compounds in Column C. Whenever the hydrogen compound is asterisked we find (*o-p*) in Column E. Whenever the hydroxyl compound is asterisked we find (*m*) in Column E. Brown and Gibson accordingly state their rule in these words: "...when X is naturally to be regarded as a derivative of HX, then C_6H_5X gives ortho- and para-derivatives; and when X is naturally to be regarded as a derivative of HOX, then C_6H_5X gives meta-derivatives." With very few exceptions (which are based upon the question of "direct oxidizability" of HX to HOX, to be considered later) the Brown and Gibson rule has been found to be capable of most rigorous application. Its authors did not look upon it as a law because there was "no visible relation to any mechanism by which substitution is carried out in one way rather than in another way."

It has been shown in detail in previous papers¹ that there is a very definite relation to a mechanism, which becomes evident when we determine the difference between X in HX and X in HOX. In the ordinary structural formulas no difference is apparent but from the electronic point of view, when H is positive and O is negatively divalent, it necessarily follows that X in HX functions negatively while X in HOX functions positively; as is evident in the electronic formulas $H \overset{+}{-} X$ and $H \overset{+}{-} O \overset{+}{-} X$.

¹ Fry, *Loc. cit.*

and Gibson assumed as their basis of classifying substituents. For instance, Holleman¹ states that the rule,

"although remarkable and representing very well many of the observed facts, does not give satisfaction since it depends entirely upon the question of the direct oxidation of the hydrogen compounds of the substituents. Thus, at the time (1892) when Brown and Gibson published their rule, methane, $\text{H}.\text{CH}_3$, could not be oxidized directly to methyl alcohol, $\text{HO}.\text{CH}_3$; hence, according to the rule, the radical CH_3 should direct the entering substituent to the ortho and para positions. But since the time of the publication of the rule, Bone has proved that the primary oxidation product of methane during combustion is methyl alcohol. As a consequence, the radical CH_3 should then direct the entering substituent to the meta position. This discovery of Bone renders the rule inexact. While it is perfectly true that one can not directly transform $\text{H}.\text{Cl}$ to $\text{HO}.\text{Cl}$, yet on the other hand no one is certain that this will always be impossible."

Therefore, Holleman contends that with the progress of science the Brown and Gibson rule becomes less and less applicable.

Now this criticism of Holleman is only apparently justified, because Brown and Gibson unfortunately based their classification of substituents upon the debatable standpoint of the direct oxidizability in one step of HX to HOX . It has been shown that the chief point of distinction between the two classes of substituents is not the direct oxidizability of HX to HOX but rather depends upon the electronic interpretation of the rule in conjunction with the electronic formula of benzene, and the fact that X in HX is negative while X in HOX is positive. These points of view invalidate Holleman's criticism of the Brown and Gibson rule.

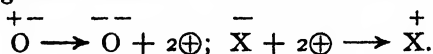
Further light may be thrown upon the nature of the substituents (X) commonly found in the benzene nucleus by considering the behavior of certain HOX compounds as oxidizing agents, and the susceptibility to oxidation of certain HX compounds, thus placing the Brown and Gibson classification on a different basis. Consider, first, a few of those substituents (OH , NH_2 , Cl and CH_3) which Brown and Gibson regarded as naturally derived from HX , not directly oxidizable to HOX . It is particularly noteworthy that the hydroxyl compounds of each of these substituents may function as an oxidizing agent while their hydrogen compounds are not oxidizing agents in the common sense of the word. Furthermore, the hydroxyl compounds of these substituents are less stable than their corresponding hydrogen compounds, *i. e.*, the entropy of the HX compound is less than the entropy of the HOX compound. When HOX functions as an oxidizing agent ($\text{HOX} \rightarrow \text{HX} + \text{O}$) yielding HX and oxygen (either free or combined) there is a change in the polarity of X from $\overset{+}{\text{X}}$ to $\overset{-}{\text{X}}$. This change may be represented as involving either an oxidation

of negative hydroxyl ions by positive chlorine ions ($\text{HO}.\text{Cl} = \text{HO} +$

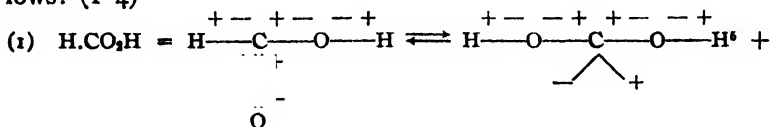
¹ Sur les regles de substitution dans le noyau benzique-Conference faite devant la Societe chimique de France, le 2 juin 1911. *Bull.*, 1911, 4e Serie 9. pp. 1-xlv.

$\overset{+}{\text{Cl}} \rightarrow \overset{+}{\text{H}} + \overset{-}{\text{Cl}} + \overset{-}{\text{O}}$ ¹ or an intramolecular oxidation and reduction
 $(\text{H} \overset{+}{-} \text{O} \overset{-}{-} \text{X} \rightarrow \text{H} \overset{+}{-} \text{O} \overset{+}{-} \text{X} \rightarrow \text{H} \overset{+}{-} \text{X} + \overset{-}{\text{O}})$ ² Now, since the compounds of the type HOX are less stable than those of the type HX, as shown by oxidation reactions, and since these oxidations involve the transition from $\overset{+}{\text{X}}$ to $\overset{-}{\text{X}}$, we may accordingly assume that $\overset{-}{\text{X}}$ is more stable than $\overset{+}{\text{X}}$.³ In other words, the tendency for X to function negatively is more pronounced than its tendency to function positively, but it may function either way as its H.X and HO.X compounds show. This may be postulated as a general property of those substituents which Brown and Gibson regarded as naturally derived from HX not directly oxidizable to HOX.

In order to complete the analysis of the Brown and Gibson rule it will be necessary to consider from the same points of view a few of those substituents, namely CO₂H, COH, SO₂H and NO₂, which were formerly regarded as belonging to the type HOX derivable by direct oxidation of HX. In fact, each of these HX compounds may be oxidized directly to the corresponding HOX compound, but it should be noted that X is a complex radical and the oxidation involves fundamental changes both in the number and polarity of the valences of certain atoms comprising these radicals. These features may be illustrated by the electronic equations for the oxidations in which oxygen as $\overset{+}{\text{O}}$ functions as the oxidizing agent through the acquisition of electrons and the consequent conversion of certain negative valences in the radical X to positive valences,⁴



The complete electronic equations for the oxidations of (1) formic acid, (2) formaldehyde, (3) sulfurous acid, and (4) nitrous acid are as follows: (1-4)



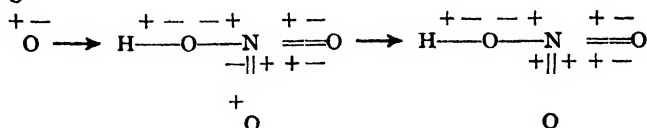
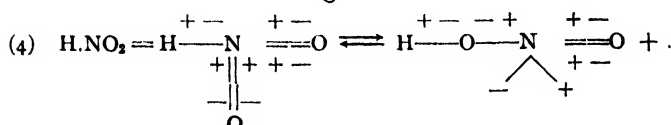
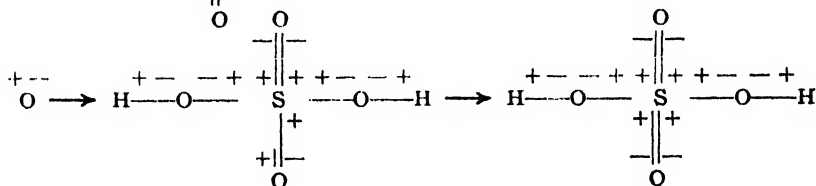
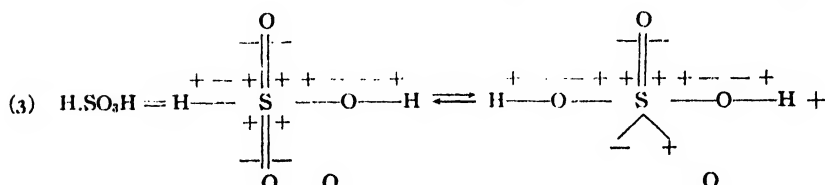
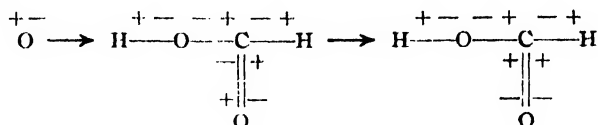
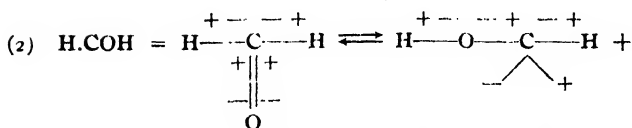
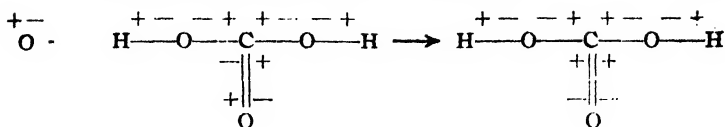
¹ For a more complete analysis of this change and the conditions under which it proceeds see Fry, *THIS JOURNAL*, 36, 267 (1914); *Ibid.*, 1044 (1914).

² Intramolecular oxidation and reduction has been described in detail by Jones, *Am. Chem. J.*, 50, 414 (1913); *THIS JOURNAL*, 36, 1268 (1914).

³ For the relation of this conception to the "nascent state" cf. Fry, *THIS JOURNAL*, 36, 272 (1914).

⁴ Oxidation and reduction reactions are presented from the positive and negative standpoint by Stieglitz, *Qual. Chem. Anal.*, Vol. 1, Chaps. XIV and XV.

⁵ This change is comparable to keto-enol tautomerism. An electronic interpretation of same has been given by Fry, *Z. physik. Chem.*, 76, 405 (1911).



The above oxidations proceed readily, in fact most of the compounds are oxidized directly by atmospheric oxygen, ($\text{O}_2 = \begin{array}{c} + - \\ \text{O} = \text{O} \\ - + \end{array} \rightarrow 2\text{O}^\cdot$). The tendency for the acid HX to change to HOX involves a change in the polarity of the complex radical X from $\begin{array}{c} - \\ \text{X} \end{array}$ to $\begin{array}{c} + \\ \text{X} \end{array}$, and accordingly X may be regarded as more stable than X^\cdot . In other words the tendency for X to function positively (HO^\cdotX) is more pronounced than its tendency to function negatively (H^\cdotX) but it may function either way as the hydrogen and hydroxyl compounds show. The above may be postulated as a general property of those substituents which Brown and Gibson re-

garded as naturally derived from HOX which results from the direct oxidation of HX.

Other points of significance may be noted in Equations 1-4 above. In formic acid, Equation 1, three of the carbon valences are positive while the fourth is negative. In carbonic acid, four carbon valences are ⁺⁻ positive. Prior to the action of O, formic acid is in equilibrium with a tautomeric modification in which the carbon atom is bivalent and shows one free positive and one free negative valence. These free valences unite ⁺⁻ with O and, either simultaneously or subsequently, the negative carbon valence is oxidized to a positive valence and oxygen ⁺⁻(O) thereby becomes ^{- -}negatively divalent (O). The tautomeric modification of formic acid, showing a free positive and a free negative valence, would through the polarization of these valences present an illustration of a bivalent carbon compound.¹ Another illustration is shown in Equation 2.

Furthermore it should be noted in Equation 3 that sulfurous acid (H.SO₃H) is ordinarily written (HO.SO₂H), in which the sulfur atom (comparable to the carbon atom above shows a free positive and a free negative valence, and the polarization of these valences renders sulfur tetravalent; but, on oxidation to sulfuric acid, the sulfur atom becomes hexavalent. In precisely the same manner nitrous acid (H.NO₂) is commonly written (HO.NO) in which nitrogen is trivalent; but oxidation to nitric acid renders nitrogen pentavalent. Now Equations 1-4 show that formaldehyde, formic acid, sulfurous acid and nitrous acid belong to the same class and same type of oxidizable compounds. Since the sulfur atom in sulfurous acid increases its valence by two on oxidation to sulfuric acid, and since the nitrogen atom in nitrous acid likewise increases its valence by two when oxidized to nitric acid, it follows, similarly, that the carbon atom in formaldehyde and in formic acid must undergo likewise an increase of two in its valence when the compounds are oxidized to formic acid and carbonic acid, respectively. In other words, this classification of the substituents and the electronic system of oxidation lends further support to and an electronic interpretation of the existence of bivalent carbon compounds.

Summary of Part III.

The extended interpretation and analysis of the Brown and Gibson rule brings out the following facts:

¹ Stieglitz (*Loc. cit.*, Vol. I, pp. 269-298) has given a detailed account of the oxidation of carbon compounds, in particular formaldehyde, showing by means of the chemometer that there is involved an actual transfer of electrical charges. The classification of sulfurous and nitrous acids with formaldehyde in the present discussion leads to the suggestion that certain sulfites and nitrites might lend themselves to similar significant demonstrations. See also Stieglitz, *Science*, 27, 774 (1908).

1. Certain substituents (OH, Cl, Br, I, NH₂, CH₃, etc.) lead to the formation chiefly of ortho and para derivatives of benzene, because their tendency to function negatively is more pronounced than their tendency to function positively. This tendency may be formulated thus: $\overset{-}{X} > \overset{+}{X}$.

2. Certain other substituents (CO₂H, COH, SO₃H, NO₂, etc.) lead to the formation chiefly of meta derivatives of benzene, because their tendency to function positively is more pronounced than their tendency to function negatively. This tendency may be formulated thus: $\overset{+}{X} > \overset{-}{X}$.

3. The objections which have been directed against the Brown and Gibson rule have been based upon the question of the direct oxidizability of HX to HOX. These objections are invalid, because the distinction between the two classes of substituents rests upon the facts summarized in paragraphs (1) and (2) above, and the fact that X in HX is negative while X in HOX is positive. These distinctions, in conjunction with the electronic formula of benzene, show why certain monosubstituted derivatives of benzene yield chiefly ortho- and para-disubstituted derivatives, while others yield chiefly meta-disubstituted derivatives.

IV. THE SIMULTANEOUS FORMATION OF ORTHO-, META- AND PARA-SUBSTITUTED DERIVATIVES OF BENZENE.

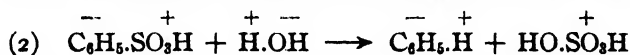
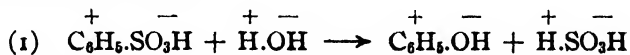
Previous papers¹ relating to substitution in the benzene nucleus from the electronic point of view have interpreted the formation of ortho and para compounds on the one hand, and meta-compounds on the other, as distinct and separate processes because, as a general rule, a given mono substituted compound yields chiefly a meta-derivative or a mixture of ortho- and para-derivatives. But in many reactions there results a mixture of ortho-, meta-, and para-disubstituted derivatives in which the quantities of the isomers vary. Consequently it becomes necessary to explain (A) the simultaneous formation of ortho-, meta- and para-disubstituted derivatives; and also (B), the simultaneous formation of polysubstituted derivatives. These explanations involve the electronic formula of benzene, the rule of substitution, and the conception of *electronic isomers or electrotomers in dynamic equilibrium, i. e., electronic tautomerism*.

The substituents (X) commonly found in the benzene nucleus were shown in Part III to function either positively or negatively according as they were derivatives of the types $\overset{-}{\text{HO}}.\overset{+}{\text{X}}$ or $\overset{+}{\text{H}}.\overset{-}{\text{X}}$, respectively. Now it has also been shown in a previous paper² that a number of these substituents may function either negatively or positively when in combination with carbon atoms of the benzene nucleus. For instance, chlorine is

¹ Fry, *Loc. cit.*, THIS JOURNAL, and *Z physik. Chem.*

² Fry, THIS JOURNAL, 36, 265 (1914).

negative in *o*- and *p*-chloronitrobenzenes, but positive in *m*-chloronitrobenzene and in 2,4,6-trichloroacyl nitrogen chloride. A particularly noteworthy example is afforded by the (SO₃H) radical, which in phenylsulfonic acid functions either negatively or positively, depending upon certain conditions. For instance, phenylsulfonic acid on hydrolysis (1) in alkaline solution yields phenol and sulfurous acid while (2) in acid solution the products of hydrolysis are benzene and sulfuric acid. Hence, the following equations:



In connection with the facts that certain substituents in the benzene nucleus may function either positively or negatively, consider the following quotation from a previous paper:¹

"The hypothesis of positive and negative valences suggests the possibility of there being at least two distinct types or electromers of a binary compound. Hence two mono substituted derivatives of benzene, $\overset{+}{\text{C}_6\text{H}_5}\overset{-}{\text{X}}$ and $\overset{-}{\text{C}_6\text{H}_5}\overset{+}{\text{X}}$, should be possible while only one is known. Therefore, if both electromers exist and only one substance is identified, it follows that the electromers are either not distinguishable by (present) physical methods, or that one electromer is transformable into the other through the transposition of electrons: $\overset{+}{\text{C}_6\text{H}_5}\overset{-}{\text{X}} \rightleftharpoons \overset{+}{\text{C}_6\text{H}_5}\text{X} \rightleftharpoons \overset{-}{\text{C}_6\text{H}_5}\overset{+}{\text{X}}$."

This quotation presented the first definition of the conception of "electronic tautomerism," that is, the existence of electromers in dynamic equilibrium.²

At the present time *tautomerism* is applied to that state of substances in which only the equilibrium mixture of the structural isomers is known. Correspondingly, the term *electronic tautomerism* is applied herewith to substances in which only the equilibrium mixture of the *electronic isomers* or *electromers* is known. From this point of view phenylsulfonic acid may be regarded as an equilibrium mixture of the electromers $\overset{+}{\text{C}_6\text{H}_5}\overset{-}{\text{X}}$ and $\overset{-}{\text{C}_6\text{H}_5}\overset{+}{\text{X}}$, and any other mono- or polysubstituted derivative of benzene may be regarded similarly, as will be shown later.

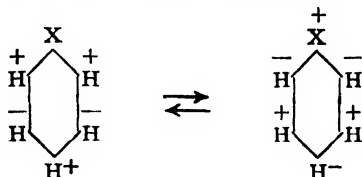
(A) The Simultaneous Formation of Ortho-, Meta- and Para-Disubstituted Derivatives of Benzene.

Electronic tautomerism of monosubstituted derivatives of benzene will

¹ Fry, *Z. physik. Chem.*, **76**, 390 (1911).

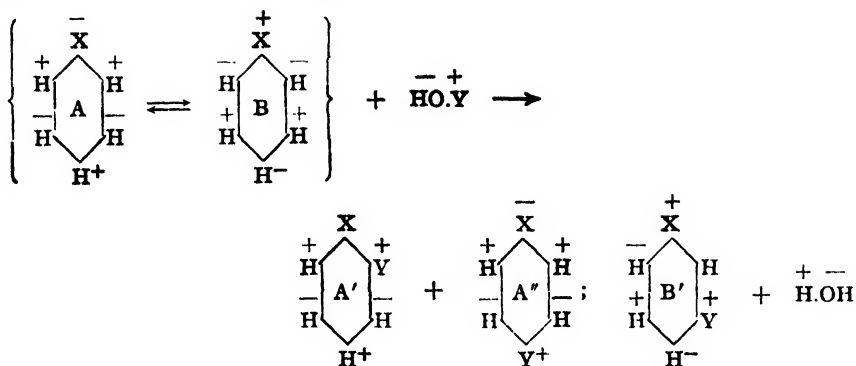
² The conception of electronic tautomerism has been applied in many significant ways. See articles by L. W. Jones (*Am. Chem. J.*, **50**, 414 (1913)); *THIS JOURNAL*, **36**, 1268 (1914); Stieglitz, *Loc. cit.*, *THIS JOURNAL*, **36**, 272 (1914); Bray and Branch, *THIS JOURNAL*, **35**, 1440 (1913); see also article on the existence of electromers of nitrogen chloride by W. A. Noyes, *Ibid.*, **35**, 767 (1913).

now be employed to explain the simultaneous formation of ortho-, meta-, and para-disubstituted derivatives of benzene. Consider any mono-substituted derivative of the general formula C_6H_5X which is now regarded as $(C_6H_5.X \rightleftharpoons C_6H_5.X)$. Indicating the polarities of the hydrogen atoms of the nucleus the equilibrium is represented thus:



Note particularly that the change in the polarity of the substituent X involves simultaneously a change in the polarities of the hydrogen atoms, but that in each electromer those atoms (or substituents) ortho and para to X are opposite in sign to X, while those atoms (or substituents) meta to X are of the same sign as X. This, of course, is the essential feature of all of the electronic formulas of benzene, namely that hydrogen atoms or substituents in positions 1, 3, and 5 of any given electromer are opposite in sign to the hydrogen atoms or substituents in positions 2, 4 and 6 of the same electromer, otherwise the symmetry, and consequently the stability, of the benzene nucleus could not be maintained. A detailed mechanism of the transpositions of electrons, the centric valences, etc., involved in the electronic tautomerism of benzene derivatives will be given later in this paper. For the present, the simpler formulas involving only the hydrogen atoms and substituents are sufficient.

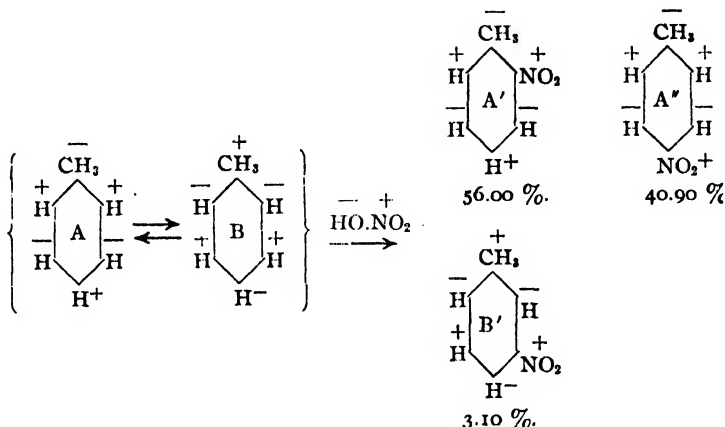
It is a well established fact that in a mixture of two isomers ($A \rightleftharpoons B$), capable of changing one into the other with such readiness that the balance between them is rapidly restored, the addition of a given substance C will result in reaction either with A, or with B, or with both A and B. If interaction occurs between A and C, B will be transformed into A on account of the disturbance of the equilibrium. The mixture then reacts as though it consisted wholly of A. If C reacts only with B, the mixture behaves, for the same reason, as though B were the only substance present. In some instances two simultaneous independent reactions may occur, namely, the interaction of A and C simultaneously with the interaction of B and C. In a precisely similar manner a given reagent, $HO.Y$, in the presence of a tautomeric mixture of electromers ($C_6H_5.X \rightleftharpoons C_6H_5.X$) may react with the one electromer or the other, or with both electromers. A complete scheme of interaction is shown in the following electronic equations:



It should be observed that if $\text{HO} \cdot \text{Y}$ reacts only with $\text{C}_6\text{H}_5 \cdot \text{X}$ (electromer A), then only ortho- and para-disubstituted derivatives (A' and A'') are formed. If $\text{HO} \cdot \text{Y}$ reacts only with $\text{C}_6\text{H}_5 \cdot \text{X}$ (electromer B), then only a meta-disubstituted derivative (B') results. If $\text{HO} \cdot \text{Y}$ interacts simultaneously with both electromers (A and B) then ortho-, meta-, and para-disubstituted derivatives (A', B' and A'', respectively) will be formed. The possibility and the extent of these reactions (as in all reactions with tautomeric substances) are dependent upon several conditions such as the solvent medium, catalytic agent, temperature, concentrations of the electromers, the speed of transition of one electromer into the other, and the respective speeds of interaction of the substituting agent with the respective electromers. These conditions are the problems which confront us in all research involving tautomers and likewise will be met in the case of electronic tautomers.

Having given a general scheme for the simultaneous formation of ortho-, meta- and para-disubstituted derivatives, one of the many examples which are in accord with and, therefore, confirm the scheme should now be considered. For instance, in the nitration of toluene, the substituent (X) already present in the nucleus is the methyl radical, which may function either positively or negatively; but in Part III it has been shown that its tendency to function negatively is more pronounced than its tendency to function positively, *i. e.*, $\text{CH}_3^+ > \text{CH}_3^-$. Hence, in the tautomeric equilibrium, $\text{C}_6\text{H}_5 \cdot \text{CH}_3^- \rightleftharpoons \text{C}_6\text{H}_5 \cdot \text{CH}_3^+$, the former electromer would predominate and interaction with $\text{HO} \cdot \text{NO}_2$ would lead to a greater yield of *o*- and *p*-nitrotoluenes than of *m*-nitrotoluene. The predominance or preponderance of the electromer $\text{C}_6\text{H}_5 \cdot \text{CH}_3^-$ over the electronic tautomer $\text{C}_6\text{H}_5 \cdot \text{CH}_3^+$ may be correlated with the speeds of re-

action with nitric acid, *i. e.*, if the former electromer reacts more rapidly than does the latter electromer, then the yield of *o*- and *p*-nitrotoluenes would exceed that of *m*-nitrotoluene.¹ These assumptions are confirmed by experimental facts, since toluene when nitrated yields 56.00% of the *o*-, 40.90% of the *p*-, and 3.10% of the *m*-nitrotoluene. The simultaneous formation of the three isomers is indicated in the following scheme:



Consider now, on the other hand, the nitration of benzoic acid. The substituent (X) already present in the nucleus is CO₂H, which may function either positively or negatively, but CO₂H⁺ > CO₂H⁻, *i. e.*, the tendency for the carboxyl radical to function positively is more pronounced than is its tendency to function negatively.² Accordingly in the equilibrium, C₆H₅·CO₂H⁺ ⇌ C₆H₅·CO₂H⁻, the latter electromer (in which the carboxyl radical is positive) would predominate, and if its speed of interaction with HO·NO₂⁺ is greater than the speed of interaction between C₆H₅·CO₂H⁻ and HO·NO₂ then the yield of *m*-nitrobenzoic acid should exceed that of the ortho and para compounds. These assumptions are confirmed by the facts, since benzoic acid on nitration yields 80.30% of the meta compound, 18.50% of the ortho, and 1.20% of the *p*-nitrobenzoic acid. The electronic equations conform to the general scheme given above.

Many other examples³ of the simultaneous formation of ortho-, meta-,

¹ The predominance of one electromer over the other may be regarded as equivalent to a greater concentration of the one electromer. Since concentration is a principle factor of the velocity of reaction, it is evident that a direct relationship exists between the predominance or preponderance of a given electromer and the velocity of the substitution reaction in which it is engaged.

² Other relationships between the properties of the carboxyl radical and its polarity are given by Fry, *THIS JOURNAL*, 36, 254-262 (1914).

³ Holleman, *Loc. cit.*, tabulations on p. 23.

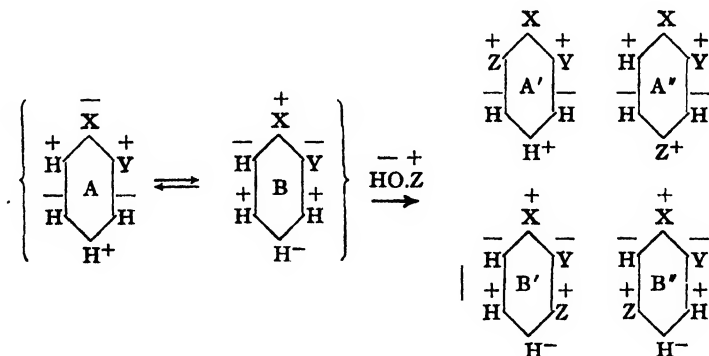
and para-disubstituted derivatives of benzene might be presented in detail. They are in complete agreement with, and accordingly confirm, the principle of the electronic tautomerism of the electromers of the benzene derivatives, the general rule for substitution, and the scheme for the simultaneous formation of ortho-, meta-, and para-disubstituted derivatives of benzene.

(B) The Simultaneous Formation of Polysubstituted Derivatives of Benzene.

The principles underlying the simultaneous formation of polysubstituted derivatives of benzene are identical with those just given in the preceding section (A), and may be illustrated by considering the introduction of a third substituent (Z) into (1) an ortho-, (2) a para-, and (3) a meta-disubstituted derivative, C_6H_4XY .

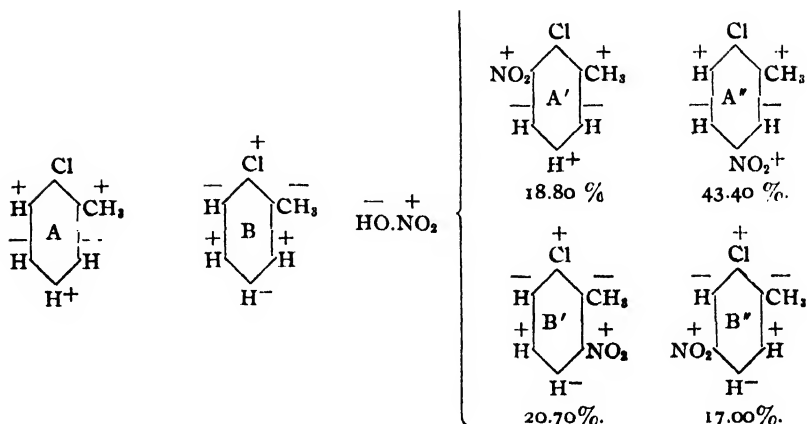
Scheme (1).—Introduction of a Third Substituent Into an Ortho-Disubstituted Derivative.

Here the electronic tautomerism involves two electromers of an ortho-diderivative. These electromers will be designated by the letters A and B while their substitution products will be indicated by A', A'', etc., and B', B'', etc., respectively. The general scheme (1) for the introduction of the third substituent Z is as follows.



Theoretically and electronically four trisubstituted isomers are obtainable, namely, A' and A'' from electromer A, and B' and B'' from electromer B. A remarkable experimental confirmation of this scheme is found in the work of Wibaut¹ who showed that the nitration at 0° of *o*-chlorotoluene yielded all four possible mononitro compounds in considerable quantity. The electronic interpretation is embodied in the following equations, which are perfectly comparable to the equations of scheme (1) above. The percentage yield of each isomer will be indicated beneath the appropriate electronic formula.

¹ Wibaut, *Recueil*, 32, 244 (1913).



In section (B) of Part III it was shown that $\text{Cl} > \text{Cl}$, and $\text{CH}_3 > \text{CH}_3$, *i. e.*, the chlorine and methyl radicals tend to function negatively rather than positively, but in *o*-chlorotoluene (either electromer, A or B) the substituents must be opposite in polarity. This leads to the consideration of a significant question, namely, will the polarities of the substituents present in the nucleus predetermine in any way the relative quantities of the isomeric derivatives which are formed? In the simultaneous formation of the isomeric disubstituted derivatives of benzene the polarities of the substituents and the tendencies of certain substituents to function in one way rather than in another way were shown to be related to the relative quantities of the isomers (ortho and para on the one hand, and meta on the other) which were formed. Now in the case of *o*-chlorotoluene the two substituents present naturally tend to function negatively, but since one must function negatively while the other functions positively another question arises, namely, is the tendency for chlorine to function negatively more pronounced than the tendency for methyl to function negatively? The answer to this important question can be derived in an indirect way by comparing the general stability of methyl alcohol ($\text{HO}\cdot\text{CH}_3$) with that of hypochlorous acid ($\text{HO}\cdot\text{Cl}$). The latter is undoubtedly the less stable, since it is readily decomposed by light or heat, whereas methyl alcohol is a comparatively stable compound. Now, the instability and decomposition of hypochlorous acid involves the change, as previously shown, from Cl to Cl , and since $\text{HO}\cdot\text{Cl}$ is less stable than $\text{HO}\cdot\text{CH}_3$, naturally it may be assumed that the tendency for chlorine to function negatively is more pronounced than the tendency for methyl to function negatively, *i. e.*, $\text{Cl} > \text{CH}_3$. Or in equivalent terms, the tendency for methyl to function positively is more pronounced than the tendency

for chlorine to function positively,¹ i. e., $\overset{+}{\text{CH}_3} > \overset{+}{\text{Cl}}$, since $\overset{-}{\text{HO}}.\overset{+}{\text{CH}_3}$ is more stable than $\overset{-}{\text{HO}}.\text{Cl}$.

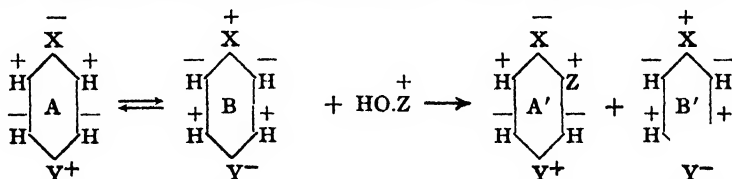
These relationships lead to the conclusion that of the two electromers (A and B) of *o*-chlorotoluene, the one (A), in which (Cl) is negative and (CH_3) is positive, would predominate, which in turn would indicate that the nitration of *o*-chlorotoluene might yield a greater quantity of the nitrochlorotoluenes A' and A'', than of the nitrochlorotoluenes B' and B''. These assumptions are confirmed by the facts, since Wibaut (*loc. cit.*) has determined the yields of the four mononitro-*o*-chlorotoluenes to which are assigned, herewith the abbreviated electronic formulas in conformity with the preceding scheme of substitution:

| | |
|---|-------|
| Electromer (A) \longrightarrow (A'), $\overset{+}{\text{C}_6\text{H}_4}.\overset{-}{\text{CH}_3}.\overset{+}{\text{Cl}}.\overset{+}{\text{NO}_2}$ (1,2,3)..... | 18.8% |
| Electromer (A) \longrightarrow (A''), $\overset{+}{\text{C}_6\text{H}_4}.\overset{-}{\text{CH}_3}.\overset{-}{\text{Cl}}.\overset{+}{\text{NO}_2}$ (1,2,5)..... | 43.4% |
| | 62.2% |
| Electromer (B) \longrightarrow (B'), $\overset{-}{\text{C}_6\text{H}_4}.\overset{+}{\text{CH}_3}.\overset{+}{\text{Cl}}.\overset{+}{\text{NO}_2}$ (1,2,6)..... | 20.7% |
| Electromer (B) \longrightarrow (B''), $\overset{-}{\text{C}_6\text{H}_4}.\overset{+}{\text{CH}_3}.\overset{-}{\text{Cl}}.\overset{+}{\text{NO}_2}$ (1,2,4)..... | 17.0% |
| | 37.7% |

The combined yields of A' and A'' total 62.2% as against 37.7%, the combined yields of B' and B''.

Scheme (2).—Introduction of a Third Substituent Into a Para-Disubstituted Derivative.

Consider now the introduction of a third substituent into a para-disubstituted derivative of benzene according to the following scheme (2):

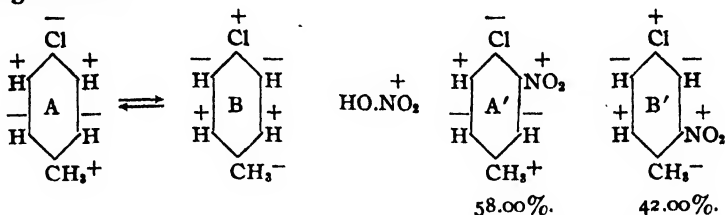


Theoretically and electronically two and only two trisubstituted derivatives are possible, namely, A' and B' from electromers A and B, respectively. One of several series of experiments which confirm the above scheme is the nitration at 0° of *p*-chlorotoluene by Holleman,² who demonstrated that only two mononitro-*p*-chlorotoluenes were produced. The

¹ The tendency for a radical to function in one way rather than in another way may be defined as its "polar stability." Other methods of determining the polar stability of a given radical will be described in a subsequent paper of this series.

² Holleman, *Recueil*, 28, 408 (1909).

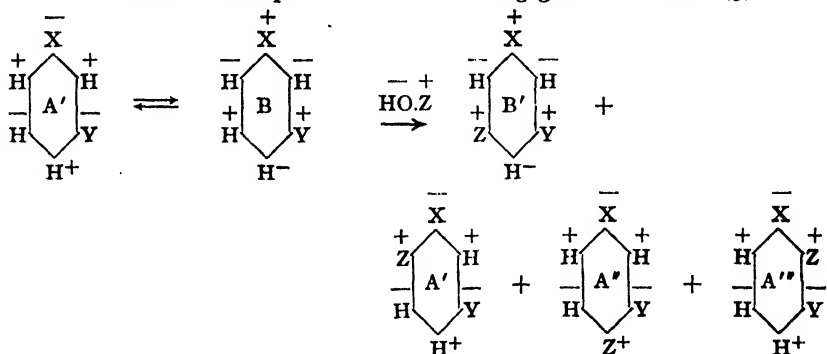
correlation of these facts with the electronic formulas is embodied in the following scheme:



Since, as previously indicated, $\text{Cl}^- > \text{CH}_3^+$ and $\text{CH}_3^- > \text{Cl}^+$, electromer A would predominate and, accordingly, the nitration of *p*-chlorotoluene would be expected to yield a greater quantity of A', $\text{C}_6\text{H}_4(\text{CH}_3)(\text{Cl})(\text{NO}_2)$ (1, 4, 3), than of B', $\text{C}_6\text{H}_4(\text{CH}_3)(\text{Cl})(\text{NO}_2)$ (1, 4, 2). This assumption also is confirmed by the actual yields, namely, 58.00% of A' and 42.00% of B'.

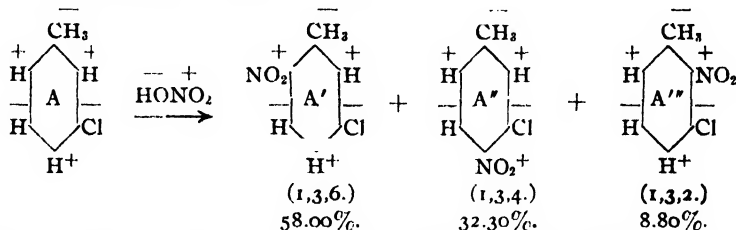
Scheme (3).—Introduction of a Third Substituent Into a Meta-Disubstituted Derivative.

The introduction of a third substituent into a meta-disubstituted derivative of benzene corresponds to the following general scheme (3):



Since the substituents X and Y occupy positions meta to each other they must be of the same polarity, *i. e.*, both are negative in A while both are positive in B. Some interesting theoretical and experimental results present themselves depending upon the tendencies of X and Y to function positively or negatively. If both X and Y belong to that class of substituents which lead to the formation chiefly of ortho and para derivatives (which is the case when $\text{X}^- > \text{X}^+$ and $\text{Y}^- > \text{Y}^+$), then electromer A would predominate and the chief substitution products would be A', A'', and A'''. Furthermore, since X and Y are meta to each other and each is naturally negative, electromer A might predominate to the exclusion of electromer B; and the introduction of a third substituent Z

would lead to the formation of only three isomeric trisubstitution products, namely, A', A'', and A'''. Just such a case is found in the nitration at 0° of *m*-chlorotoluene by Wibaut (*loc. cit.*). The percentage yields of the isomers are indicated in the scheme:



Now it has been shown that the tendency for chlorine to function negatively is more pronounced than the tendency for methyl to function negatively, *i. e.*, $\text{Cl} > \text{CH}_3$. This leads to the assumption that the entering positive nitro radical would be more subject to the directing influence of Cl than of CH_3 . Now Cl directs NO_2 to the para position rather than to the ortho position, since chlorobenzene on nitration yields 69.90% of *p*-nitrochlorobenzene and 30.10% of *o*-nitrochlorobenzene. On the other hand, CH_3 directs NO_2 to the ortho position rather than to the para positions since toluene on nitration yields 56.00% of the *o*- and 40.90% of the *p*-nitrotoluene. Accordingly, when *o*-chlorotoluene is nitrated, one should expect the greatest yield to be that of isomer (A') in which NO_2 occupies a position para to Cl and ortho to CH_3 . A smaller yield would be predicted for that isomer (A'') in which NO_2 is ortho to Cl and para to CH_3 . The smallest yield would be predicted for the isomer (A''') in which NO_2 is ortho to Cl and ortho to CH_3 . These assumptions are fully confirmed by the facts since the respective yields of the three isomers, A', A'', and A''', are, respectively, 58.00%, 32.00%, and 8.80%.¹

Returning again to the general scheme (3) above, it should be noted that if X and Y belong to that class of substituents which lead to the formation chiefly of meta derivatives, which is the case when $\text{X} > \text{X}^+$ and $\text{Y} > \text{Y}^+$, then electromer B would predominate. Accordingly, the introduction of a third substituent Z would lead to the formation chiefly of the trisubstitution product in which all three substituents (X, Y and Z) are positive. Many examples are found in the literature which show that

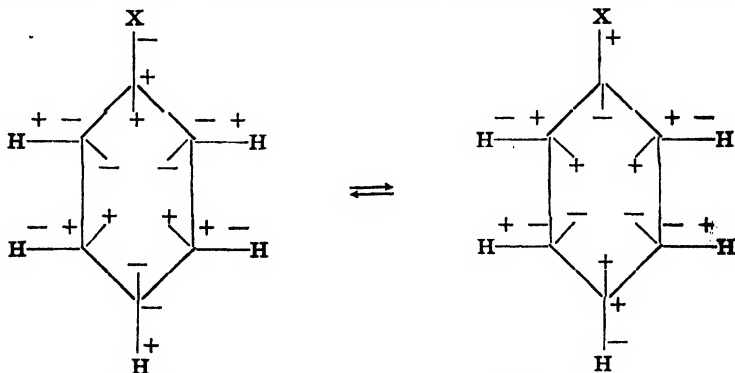
¹ This constitutes a further proof that the polarities of the substituents in the nucleus and their tendencies to function in one way rather than in another way predetermine not only the type of substitution but also the relative quantities of the isomers produced.

when the substituents in the nucleus are positive, the entering substituent assumes a position meta to those present, and the predominating isomer corresponds to B', the derivative of electromer B. Exact quantitative data upon the amounts of the other possible isomers have not been found in the literature.

Having considered all of the possibilities which might be encountered in the introduction of a third substituent Z into an ortho-, a para-, and a meta-disubstituted derivative, C_6H_4XY , of benzene, and having shown that experimental facts and data are in agreement with the theoretical deductions, with the electronic formulas, and the principle of electronic tautomerism, and with the general electronic rule for substitution, it should be added that the formation of other poly-substituted derivatives of benzene will conform in general to the principles and rule previously developed and illustrated. This claim is warranted by a careful study of the numerous tables of the variously substituted derivatives of benzene which have been compiled with great care and presented by Holleman in his extended work¹ on the influence of the substituents in the benzene nucleus, and the principles of substitution.²

(C) The Mechanism of Electronic Tautomerism of Benzene Derivatives.

The important part played by the principle of electronic tautomerism in the explanation of substitution in the benzene nucleus leads to the consideration of a mechanism which involves the centric valences of the carbon atoms of the nucleus. The key to this mechanism is embodied in the assumption (to be substantiated by experimental facts) that when a given hydrogen atom or substituent is negative it is united to a carbon atom which possesses a positive centric valence. On the other hand, when a hydrogen atom or substituent is positive it is united to a carbon atom which possesses a negative centric valence. These assumptions are embodied in the following formulas illustrating more completely



¹ Die direkte Einführung von Substituenten in den Benzolkern.

² Sur les règles de substitution dans le noyau benzique (*Loc. cit.*).

the electronic tautomerism of a monosubstituted derivative. The electronic tautomerism of a polysubstituted derivative would conform to the same principles and scheme.

When $\overset{-}{X}$ becomes $\overset{+}{X}$ ($\overset{-}{X} \longrightarrow \overset{+}{X} + 2\ominus$) the polarity of the carbon valence binding X is changed from positive to negative, *i. e.*, in terms of the electronic conception of oxidation and reduction, the positive valence has been reduced to a negative valence. On the other hand, when $\overset{+}{X}$ becomes $\overset{-}{X}$, the valence binding X is changed from negative to positive, *i. e.*, it is oxidized. Simultaneously, corresponding changes occur in the polarities of each of the other hydrogen atoms or substituents and the carbon valences binding same. In other words, for each oxidation there is a corresponding reduction; otherwise, the symmetry and consequently the stability of the benzene nucleus would be destroyed.¹

Another important point to be observed in the above scheme is that the transition from the one electromer to the other involves a change in the polarity of each centric valence. This type of change has been defined as "centric rearrangement." A complete scheme of the several possible centric formulas of benzene and their transitions to the Kekulé formulas has been shown to involve changes from double bonds of the type $\overset{+}{C}=\overset{-}{C}$, defined as "contraplex," to double bonds of the type $\overset{-}{C}=\overset{+}{C}$, defined as "diplex." Such changes, "contraplex-diplex transitions," take place in those compounds which show distinct bands in their absorption spectra.² Accordingly, they serve as a structural basis for the relationship between chemical constitution and absorption spectra. In other words, the rearrangements of the centric valences and the concomitant contraplex-diplex transitions cause a disturbance in the vibrations of the systems of electrons, whereby light of correlated period is absorbed in accordance with the theory of resonance. By means of the various electronic formulas of benzene and their systems of dynamic equilibria, I have been able to demonstrate that a definite relationship exists between the oscillation frequencies of the seven bands in the absorption spectrum of benzene and the numbers of contraplex-diplex transitions involved, which function as the origin of the respective absorption bands. This relationship is that of a linear function expressed by the equation, $\gamma = 21.60628x + 3679.509$, in which (γ) is the oscilla-

¹ An explanation of the stability of the benzene nucleus based upon the fact that the number of positive hydrogen atoms of the nucleus must be equal to the number of negative hydrogen atoms, is given by Fry, *THIS JOURNAL*, 36, 270 (1914).

² The definitions and principles indicated in this paragraph are fully described in a paper on the absorption spectra of benzene, Fry, *Z. physik. Chem.*, 76, 398 (1911).

tion frequency of a given band, and (x) is the number of contraplex-diplex transitions functioning as the origin of the given band. The deviations of the calculated frequencies from the observed frequencies were less than the limits of error in experimental observation. Other similar and exact relationships were developed and found to hold for the oscillation frequencies of the absorption bands of naphthalene,¹ chlorobenzene and bromobenzene,² and for the fluorescence bands of anthracene and phenanthrene.³ This work has been briefly indicated here because through these physical measurements an experimental confirmation is offered for the hypothesis of contraplex-diplex transitions which involve centric rearrangements, *i. e.*, changes in the polarities of the centric valences of benzene. These centric valences and rearrangements will now be shown to play a very definite part in the further development of the mechanism of substitution on the benzene nucleus.

(D) The Mechanism of Substitution in the Benzene Nucleus and an Electronic Interpretation of the Hypothesis of Holleman.

Holleman in his work on "Die direkte Einführung von Substituenten in den Benzolkern" has described and discussed the various hypotheses which have been advanced at different times to explain the rules of substitution, but he is of the opinion that none of these hypotheses are able to give a satisfactory explanation of the facts. Furthermore, Holleman, in a very recent paper⁴ makes this statement:

"Notwithstanding the fact that the problem of substitution in the benzene nucleus has been studied intensively enough of late, there still remains a fundamental question which has not yet been solved; it is the question of knowing the reason why such or such group directs a new substituent chiefly to the para-ortho positions or chiefly to the meta position."

A propos of this statement, it has been shown in Part III, Section B, of this series of papers (and in previous papers) that the electronic formula of benzene and the electronic interpretation of the Brown and Gibson rule afford an explanation, in the sense that if the substituent in the nucleus is negative then the entering positive substituent must assume a position either ortho or para to the substituent already present; and, if the substituent in the nucleus is positive, then the entering positive substituent must assume a position meta to the one already present. This hypothesis has been substantiated by numerous examples of substitution. The mechanism, or schemes, for these reactions as previously presented involved the simplified electronic formulas for benzene indicating only the polarities of the hydrogen atoms and substituents,

¹ Fry, *Z. physik. Chem.*, **76**, 591 (1911).

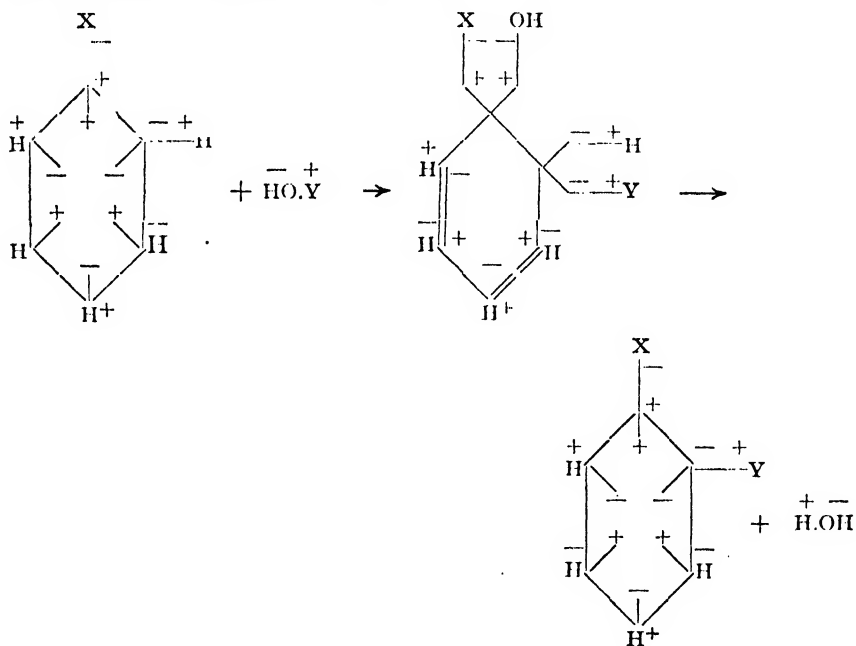
² Fry, *Ibid.*, **82**, 665 (1913).

³ Fry, *Ibid.*, **80**, 29 (1912).

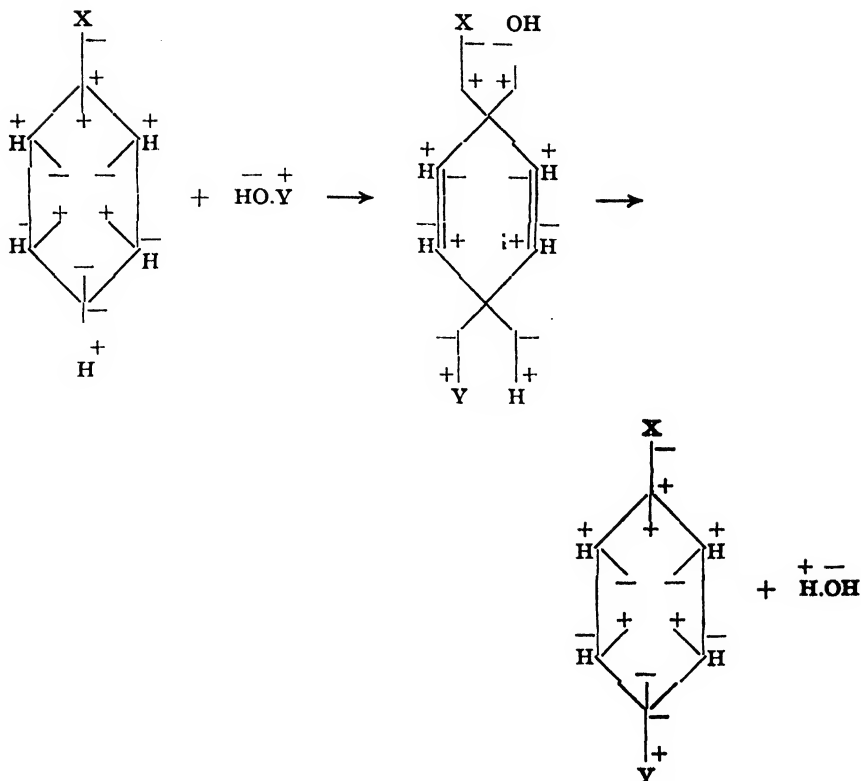
⁴ *Recueil*, **33**, 1 (1914).

and the electronic formulas of the substituting reagents; but, since it is generally conceded that substitution in the nucleus involves (1) the addition of the substituting reagent (for example, $\overset{-}{\text{HO}}.\overset{+}{\text{Y}}$) and (2) the elimination of certain elements (for example, $\text{H}.\text{OH}$), it follows that any mechanism proposed to account for these changes (1 and 2) must consider the part played by the centric valences or the double bonds of the nucleus. For the present, it is simpler to indicate the part played by the free centric valences in effecting the addition of the substituting reagent, rather than to picture the part as played by the "opening up" or "breaking" of the double bonds. In either case, the mechanism of the change involved would amount to one and the same thing, since the centric formula is simply an intermediate phase between those Kekulé formulas or phases which possess double bonds.

From the above points of view a more complete mechanism of substitution will be indicated; first, for the formation of an ortho-disubstituted derivative, in which case the substituent (X) present in the nucleus functions negatively and the entering substituent (Y) is positive. The formulas will indicate only the polarities of the bonds or valences which are immediately related to the particular changes.

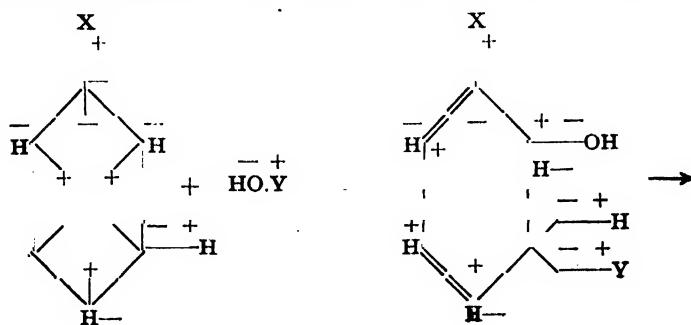


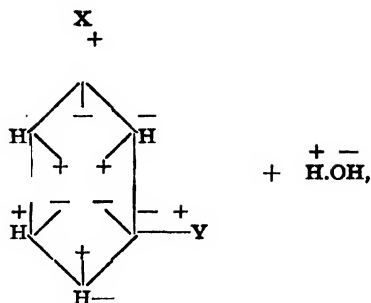
The formation of a para-disubstituted derivative also involves the electrophile in which X is negative and the entering substituent Y, positive.



On the other hand, the formation of a meta-disubstituted derivative involves the electromer in which X is positive and the entering substituent Y is positive.

In each of the above schemes, the addition of the radicals of the substituting reagent (HO and Y) engages only two of the six centric valences. The remaining centric valences lend themselves to the formation of double bonds in the addition product. This addition reaction is followed by the





elimination of $\overset{+}{\text{H}}$ and $\overset{-}{\text{OH}}$ as water and a consequent return to the centric formula of the disubstituted derivative.

The substitution of halogen ($\text{Y}_2 = \overset{+}{\text{Y}} + \overset{-}{\text{Y}}$) would correspond to the addition of $\overset{+}{\text{Y}}$ and $\overset{-}{\text{Y}}$ to the centric valences with the subsequent elimination of $\overset{+}{\text{H}}\cdot\overset{-}{\text{Y}}$ and the fixing of $\overset{+}{\text{Y}}$ in the nucleus either ortho or para to $\overset{+}{\text{X}}$, or meta to $\overset{+}{\text{X}}$. In paper II of this series (*loc. cit.*) a mechanism was given for the action of halogen carriers in effecting nucleus substitution which is also readily correlated with the above schemes. The halogen carrier forms an unstable addition compound with the radicals $\overset{+}{\text{Y}}$ and $\overset{-}{\text{Y}}$ of the halogen molecule Y_2 . This unstable addition compound either induces the direct combination of $\overset{+}{\text{Y}}$ and $\overset{-}{\text{Y}}$ with centric valences, or the dissociation products of the addition compound itself combine with the centric valences. In either event, subsequent elimination of $\overset{+}{\text{H}}\cdot\overset{-}{\text{Y}}$ and the carrier results in the nucleus substitution of $\overset{+}{\text{Y}}$.

An examination of the preceding mechanisms of substitution shows that the *polarity of the substituent X present in the nucleus and the polarities of the centric valences predetermine the types of substitution which result in the formation either of ortho- and para-derivatives, or of meta-derivatives.* If both electromers ($\text{C}_6\text{H}_5\cdot\overset{+}{\text{X}}$ and $\text{C}_6\text{H}_5\cdot\overset{-}{\text{X}}$) interact with $\text{HO}\cdot\overset{+}{\text{Y}}$, simultaneous formation of ortho-, para-, and meta-derivatives follows as previously described and confirmed by extended experimental facts and data.

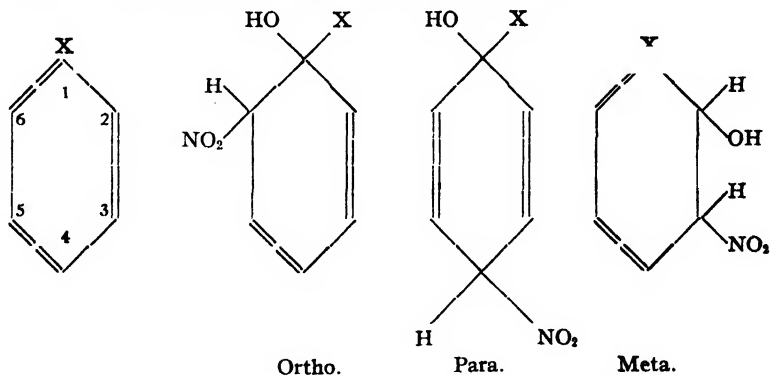
It may now prove interesting to show that the mechanism for the formation of ortho-para and meta classes of derivatives as proposed by Holleman may be correlated with the electronic formulas and substitution schemes presented in this paper.

On the basis of the Kekulé formula (the centric formula would apply equally well) Holleman supposes that the substituent X, already present in the nucleus, may either promote or retard the addition of the radicals

of the substituting reagent to the double bonds (or centric valences). If X promotes addition, the ortho and para compounds are formed, addition having taken place in position 1,2 (or 1,6) and 1,4, respectively. Conjugation is assumed to cause the addition in the para (1,4) position according to Thiele's hypothesis. On the other hand, the addition of the substituting reagent to the double bond (or centric valences) of carbon atoms 2 and 3 cannot be greatly influenced by X, because X is not in direct relation with these atoms. In other words, under the influence of X, the speed of addition to position 1,2 (or 1,6) and 1,4 is either accelerated or retarded, while the speed of addition to position 2,3 (or 5,6) is about the same as in the nonsubstituted benzene itself. Accordingly, when X accelerates the reaction, substitution takes place in positions ortho and para; when the acceleration is great, the ortho and para products will be formed exclusively, for the quantity of the meta product which could be formed simultaneously through addition to position 2,3 is then so small that it is not perceptible. When, on the other hand, the acceleration is not so great, the meta isomer may also be formed.

In the case where X retards the reaction, the addition to position 2,3 predominates and proceeds more rapidly than the addition to position 1,2 (or 1,6) and 1,4. The meta isomer then becomes the principal product.

Holleman illustrates the mechanism of these types of addition by supposing C_6H_5X to undergo nitration, in which case nitric acid adds as HO and NO_2 . The addition compounds are as follows:



By the subsequent removal of H and OH as water, an ortho, a para or a meta compound is formed.

Now it should be noted that the above addition compounds as formulated by Holleman are identical with the electronic formulas for the addition compounds previously indicated, but with this important exception: the electronic formulas, by indicating the polarities of the hydrogen atoms, the substituents, the centric valences, and the radicals of the substituting reagent, make possible a formula-mechanism by which addition must take

place in one way rather than in some other way. On the other hand, the ordinary Kekulé and centric formulas cannot, *per se*, indicate why addition should proceed in one way rather than another. For instance, the addition of HO.NO_2 in Holleman's scheme unites OH to carbon atom 1, and NO_2 to carbon atom 6. Now as far as the regular Kekulé or centric formula is concerned OH might just as well unite to atom 6 while NO_2 unites to atom 1. Other additions are structurally possible in positions 1,4 and 2,3. In other words, six types of addition instead of the three as indicated by Holleman are possible from the standpoint of the ordinary structural formulas. Hence, it is evident that some qualification or limitation of the types of addition must be made. This, of course, is true of any hypothesis which deals with structural formulas and proposed mechanisms of reaction, but the marked superiority of electronic formulas over ordinary structural formulas lies in the fact that the valences of the atoms and radicals may be qualified, in conformity with facts of experiments, as positive or negative, a distinction which cannot be embodied in the ordinary formulas. Therefore, a valence hypothesis which permits of such qualifications possesses greater significance in the interpretation of chemical phenomena than the ordinary valence hypothesis.

It may now be demonstrated that Holleman's formulas for the ortho, para, and meta addition compounds may be interpreted in terms of positive and negative valences. Furthermore, this interpretation logically leads to the same electronic formulas that were proposed for these addition compounds in the first part of this section (D). This necessarily follows if we admit that the electronic formulas of water and nitric acid are $\overset{+}{\text{H}}.\overset{-}{\text{O}}\text{H}$ and $\overset{-}{\text{H}}\text{O}.\overset{+}{\text{N}}\text{O}_2$, respectively; and, that the benzene molecule is symmetrically constituted, *i. e.*, from the electronic point of view that for every positive charge or valence there is a corresponding negative charge or valence. The correlation of Holleman's formulas with the electronic formulas is as follows:

In Holleman's ortho addition compound, the union of $\overset{-}{\text{O}}\text{H}$ with carbon atom 1 and $\overset{+}{\text{N}}\text{O}_2$ with carbon atom 2 or 6 means that the free valence of atom 1 is positive while that of atom 2 or 6 is negative. In the para addition compound, $\overset{+}{\text{N}}\text{O}_2$ unites to carbon atom 4 which, accordingly, possesses a free negative valence. In other words, the ortho and para addition compounds show that the centric valences of positions 2, 4, and 6 are negative while 1 is positive. Consequently, from the symmetry standpoint, the centric valences of positions 3 and 5 are positive just as 1 is positive.

The polarities of the hydrogen atoms and substituents of the nucleus are indicated by Holleman's assumption that the disubstituted derivative

is formed through the elimination of water, $\overset{+}{\text{H}}\text{.}\overset{-}{\text{OH}}$. In Holleman's formula for the ortho addition compound, the hydrogen atom of position 2 or 6 is eliminated with the hydroxyl radical of position 1; and in the para addition compound the hydrogen atom of position 4 is likewise eliminated with hydroxyl of position 1. Since the elimination of water is the union of $\overset{+}{\text{H}}$ and $\overset{-}{\text{OH}}$, it follows that the hydrogen atoms of positions 2, 4, and 6 of the ortho and para nitrocompounds of Holleman are positive. Consequently, from the symmetry standpoint, the hydrogen atoms or substituents of position 1, 3, and 5 are negative. As a matter of fact, the ortho and para nitrocompounds, in which $\text{X} = \text{Cl}$ or Br , readily exchange X for hydroxyl on treatment with aqueous potassium hydroxide: since OH is negative, X is accordingly negative.

Having correlated Holleman's ortho and para compounds with the electronic formulas, consider, on the other hand, his formula for the meta addition compound. Here, HO unites with the free valences of carbon atoms 2 or 6, while NO_2 combines with those of atoms 3 or 5. Hence, the free or centric valences of positions 2 and 6 are positive while those of positions 3 and 5 are negative; and from the electronic symmetry standpoint, the remaining centric valences of positions 1 and 4 must be negative and positive, respectively. Thus in the meta nitrocompound the centric valences of carbon atoms 1, 3, and 5 are negative while those of atoms 2, 4 and 6 are positive. Considering the polarities of the hydrogen atoms and substituents, NO_2 replaces the hydrogen atom of position 3 or 5, which is accordingly positive. From the symmetry standpoint X of position 1 should also be positive. As a matter of fact, when $\text{X} = \text{NO}_2$, as in nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$), the entrance of a second NO_2 is in positions 3 or 5, meta to position 1. Furthermore, when $\text{X} = \text{Cl}$ or Br in the meta nitrocompounds, X is not directly replaceable by negative hydroxyl and is presumably positive. The atoms of positions 1, 3 and 5 being positive, those of positions 2, 4 and 6 are negative.

From the above it is evident that Holleman's formulas and mechanism of substitution may be interpreted in terms of positive and negative valences, and the electronic formulas thereby developed are correlated with the electronic formulas and principles previously presented. Therefore, the numerous cases of substitution which have been interpreted by Holleman's hypothesis are also interpreted by the electronic formulas and principles which possess the added significance of showing why certain substituents (which are negative) lead to the formation of ortho- and para-derivatives, while others (which are positive substituents) lead to the formation of meta-derivatives.

The remaining features of Holleman's substitution hypothesis to be considered from the positive and negative viewpoint relate to the velocities of the substitution reactions and their dependence upon the nature of the substituents which are present in the nucleus. Thus, when a substituent, X, accelerates the substitution reaction, substitution follows the ortho-para rule which may lead to the exclusion of any meta compound. If X has no such accelerating effect, smaller or larger quantities of the meta compound will be formed. These facts make it possible to predict the place that a third substituent C will occupy in the nucleus of a disubstituted derivative, C_6H_4AB . This place is determined by Holleman by measuring the speeds of substitution of C in C_6H_5A and in C_6H_5B , and by ascertaining the proportions in which the isomers of C_6H_4AC and C_6H_4BC are formed in each case. A comparative study from these points of view enables Holleman to determine the relative effects of different substituents upon the speeds of substitution reactions. Thus, one substituent, HO, is found to have a greater accelerating effect than another, NH_2 (represented thus, $OH > NH_2$); and a comparison of these relative effects leads to a series. For instance, the substituents which lead to the formation of ortho- and para-derivatives are arranged thus: $OH > NH_2 > \text{halogens} > CH_3$. The substituents which lead to the formation of meta-derivatives present the series: $CO_2H > CHO > SO_3H > NO_2$.

A *propos* of his hypothesis, Holleman has just recently stated¹ that the cause for the different accelerating effects of the different substituents has not yet been explained. This "cause" may be interpreted in terms of the electronic conception of positive and negative valences, since I have shown that the types of substitution are directly related to the polarities of the substituents present in the nucleus and the tendencies of these to function in one way rather than in another way. For instance, as shown in Part III, those substituents which lead chiefly to the formation of ortho- and para-derivatives are the substituents which tend to function negatively rather than positively ($\overset{-}{X} > \overset{+}{X}$), while those substituents which lead chiefly to the formation of the meta compound are the very substituents which tend to function positively rather than negatively ($\overset{+}{X} > \overset{-}{X}$). Moreover, a substituent which is naturally negative may manifest a greater tendency to function negatively than another negative substituent, thus ($\overset{-}{X} > \overset{-}{Y}$); and analogously for positive substituents there exists the relation ($\overset{+}{X} > \overset{+}{Y}$). These respective tendencies were shown in Sections A and B of Part IV to account for the preponderance of one electromer over another in the electronic tautomerism of benzene derivatives. This preponderance or increased concentration, in turn, accounted for the rela-

¹ *Recueil*, 33, 1 (1914).

tive yields of the several possible isomers. Therefore, if the greater concentration of one electromer in the equilibrium system is determined by the tendencies of its substituents to function in one way rather than in another way, and since the speed of a reaction is a factor of the concentrations of the interacting substances, it follows that the speed of a substitution reaction is dependent upon the polarities of the substituents present in the nucleus and their respective tendencies to function in certain ways. From this point of view it follows that Holleman's series

($\text{OH} > \text{NH}_2 > \text{halogens} > \text{CH}_3$) may be represented thus: $\text{OH} > \text{NH}_2 > \text{halogens} > \text{CH}_3$. The other series is as follows: $\text{CO}_2\text{H} > \text{CHO} > \text{SO}_3\text{H} > \text{NO}_2$.

If the tendency for a substituent to function in one way rather than in another way be defined as the "polar stability of the substituent," it follows that the velocities of substitution reactions in the benzene nucleus are functions of the polar stabilities of the substituents of the nucleus. In other words, the polar stabilities of the substituents determine the concentrations of the electromers, which concentrations are the principle factors in determining the velocities of the substitution reactions.

A summary of Part IV may be omitted since the several topics discussed have been presented in separate sections with contents indicated. This paper, however, should be concluded with the following general statements: The conception of the electronic tautomerism of the derivatives of benzene furnishes an explanation of (1) the types of substitution and the simultaneous formation of ortho-, para-, and meta-substituted derivatives; (2) it renders possible the prediction of the relative yields of the isomers which are dependent upon the preponderance or increased concentration of one electromer over the other; (3) the concentrations of the electromers are predetermined by the "polar stabilities" of the substituents in the nucleus; (4) the velocities of substitution reactions are functions of the polar stabilities of the substituents. Accordingly all facts that are explained in terms of the velocities of reactions may be interpreted in terms of the polar stabilities of the substituents. This phase of substitution in the benzene nucleus will be considered in detail in a subsequent paper.

V. A REPLY TO A. F. HOLLEMAN.

In a recent paper¹ entitled "Substitution in the Benzene Nucleus," Dr. A. F. Holleman has taken exceptions to the electronic formula for benzene and the general rule for substitution; and has offered a number of objections. In view of the principles developed in the preceding

¹ THIS JOURNAL, 36, 2495 (1914).

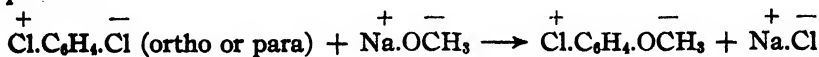
Part III, and the many applications of the conception of the electronic tautomerism of benzene derivatives presented in Part IV, it may now be shown that the chief objections offered by Holleman actually confirm and substantiate the electronic formulas for benzene and the rule for substitution. Other incidental objections will be considered in course of the reply.

In Holleman's paper the several objections are presented in separate paragraphs numbered 1-6. The present reply will consider the contents of each of these paragraphs in the same order.

(1) Holleman's first objection is directed against the assumption that monochlorobenzene may be an equilibrium mixture of two tautomeric electromers, $\overset{+}{\text{C}_6\text{H}_5}\overset{-}{\text{Cl}}$ and $\overset{-}{\text{C}_6\text{H}_5}\overset{+}{\text{Cl}}$. Granting such to be the case, Holleman maintains that if $\overset{+}{\text{C}_6\text{H}_5}\overset{-}{\text{Cl}}$ is stable, $\overset{-}{\text{C}_6\text{H}_5}\overset{+}{\text{Cl}}$ would be unstable. This I also admit provided we qualify this stability or instability in terms of the tendency for chlorine to function negatively rather than positively, *i. e.*, $\overset{-}{\text{Cl}} > \overset{+}{\text{Cl}}$, which tendency explains the preponderance or greater concentration of the one electromer over the other and the consequent increase in its reaction velocity. But to Holleman's statement that

("in *o*- $\text{C}_6\text{H}_4\text{Cl}_2$ and *p*- $\text{C}_6\text{H}_4\text{Cl}_2$, where one atom is negative and the other positive, we have perfectly stable compounds,")

the reply may be made that the existence of a perfectly stable compound is questionable. Stability is only a relative term and a given compound, so to speak, may be perfectly stable under one set of conditions, but unstable under others. Furthermore, a given atom or radical may be reactive in one compound but nonreactive in another: for example, the replacement of chlorine in *o*- and *p*-chloronitrobenzene by OH on interaction with K.OH ; and the nonreplacement of chlorine in *m*-chloronitrobenzene under the same conditions. Again, in one and the same compound such as *o*- and *p*-dichlorobenzene (compounds which Holleman regards as perfectly stable) there exist differences in the reactivities of their chlorine atoms, depending upon one being positive while the other is negative. This is evidenced by the fact demonstrated by de Mooy in Holleman's laboratory that each of these compounds exchanges one chlorine for OCH_3 on interaction with sodium methylate. This difference in the reactivities of the chlorine atoms is illustrated by the following electronic equation:



In this connection it should be noted that if halogen (X) is introduced into the benzene nucleus (either through interaction with HO.X or through

the action of a halogen carrier such as SbX_3) the resultant electromer $\text{C}_6\text{H}_5\text{X}^+$ would revert chiefly to the tautomer $\text{C}_6\text{H}_5\text{X}^-$, because of the tendency $\text{X}^- > \text{X}^+$. This tendency for X to function negatively rather than positively is a distinctive property and should not be confused with the replaceability of X by OH or by OCH_3 .

Again, Holleman maintains that if chlorobenzene is a mixture of $\text{C}_6\text{H}_5\text{Cl}^+$ and $\text{C}_6\text{H}_5\text{Cl}^-$, the nitration of such a mixture ought to yield *o*- and *p*-chloronitrobenzenes (derived from $\text{C}_6\text{H}_5\text{Cl}^+$) and *m*-chloronitrobenzene (derived from $\text{C}_6\text{H}_5\text{Cl}^-$), when, in reality, only the ortho- and para-disubstituted compounds are formed. In reply, recall the facts presented in Part IV, Sections A and B, showing that $\text{Cl}^- > \text{Cl}^+$, which tendency accounts for the preponderance or increased concentration of $\text{C}_6\text{H}_5\text{Cl}^-$ over $\text{C}_6\text{H}_5\text{Cl}^+$. Accordingly, the speed of interaction of the former electromer with nitric acid would exceed that of the latter electromer. Now in terms of Holleman's own hypothesis on the speeds of reaction and type of substitution, if the speed of substitution is sufficiently great, *o*- and *p*-chloronitrobenzenes would be formed to the exclusion of the meta compound. Therefore, Holleman's experimental demonstration that chlorobenzene yields only *o*- and *p*-chloronitrobenzenes may be accepted as proof that in the tautomeric equilibrium, $\text{C}_6\text{H}_5\text{Cl}^+ \rightleftharpoons \text{C}_6\text{H}_5\text{Cl}^-$, the former electromer interacts exclusively with $\text{HO}\cdot\text{NO}_2$. In contending that both electromers must interact with nitric acid, Holleman has disregarded the general principle that in a tautomeric equilibrium mixture, either one or the other, or both tautomers may interact with a given reagent. See Part IV, Section B, third paragraph, for further description and electronic equations.

(2) In his second paragraph Holleman states that:

"Fry maintains that the iodine is positive in iodobenzene, since it is formed from sodium benzoate and iodine chloride, the latter having the formula $\text{Cl}-\text{I}^+$. But iodobenzene also yields para and ortho compounds on nitration, just as the other halogen-benzenes, though in these the halogen is admitted to have a negative charge."

In reply, Holleman has misstated me with reference to iodobenzene since the reaction in question is that of $\text{Cl}-\text{I}^+$ upon silver benzoate (not sodium benzoate)¹ showing that the iodine atom in iodobenzoic acid (and not iodobenzene) is positive. The nitration of iodobenzene from the electronic point of view is identical with the nitration of the other

¹ As described in THIS JOURNAL, 36, 254-255 (1914).

halogen-benzenes, $\overset{+}{\text{C}_6\text{H}_5}\text{X} \rightleftharpoons \overset{-}{\text{C}_6\text{H}_5}\text{X}$, in which the former electromer may predominate to the exclusion, of the latter, whereupon only ortho- and para-derivatives are formed.

Further, Holleman states:

"It is somewhat striking that Fry admits on p. 252, *Loc. cit.*, that chlorobenzene has the formula $\overset{-}{\text{C}_6\text{H}_5}\text{Cl}$, whereas he declares on p. 264, that it has been impossible so far to prove directly, whether the chlorine atom in monochlorobenzene is positive or negative."

In reply, the first part of the above statement is a misinterpretation since my original statement was as follows (*loc. cit.*, pp. 251-2): "According to the principles previously developed from the Crum $\overset{+}{\text{C}_6\text{H}_5}\text{Cl}$ and Gibson Rule, the electronic formula of chlorobenzene is $\overset{-}{\text{C}_6\text{H}_5}\text{Cl}$ while that of nitrobenzene is $\overset{+}{\text{C}_6\text{H}_5}\text{NO}_2$." In other words, chlorobenzene is a derivative of $\overset{+}{\text{H}}\text{Cl}$ from the standpoint of the Brown and Gibson Rule, and, accordingly, is regarded as $\overset{+}{\text{C}_6\text{H}_5}\text{Cl}$. In the further development of this rule and the electronic tautomerism of benzene derivatives, chlorobenzene is $\overset{+}{\text{C}_6\text{H}_5}\text{Cl} \rightleftharpoons \overset{-}{\text{C}_6\text{H}_5}\text{Cl}$. My statement (*loc. cit.*, p. 264): "it has been impossible so far to prove directly whether the chlorine atom in monochlorobenzene is positive or negative"—was made with reference to the possibility of hydrolyzing chlorobenzene so as to obtain: (1) from $\overset{+}{\text{C}_6\text{H}_5}\text{Cl}$, the products $\overset{+}{\text{C}_6\text{H}_5}\text{OH}$ and $\overset{-}{\text{H}}\text{Cl}$; and (2) from $\overset{-}{\text{C}_6\text{H}_5}\text{Cl}$, the products $\overset{-}{\text{C}_6\text{H}_5}\text{H}$ and $\overset{+}{\text{HO}}\text{Cl}$. This has not been possible with chlorobenzene but similar hydrolyses have been accomplished with benzene sulfonic acid (*loc. cit.*, p. 265).

The objections presented in paragraph (2) are thus shown to involve a misstatement and a misinterpretation neither of which invalidates the electronic formula for benzene or the rule for substitution.

(3) In his third paragraph Holleman states that:

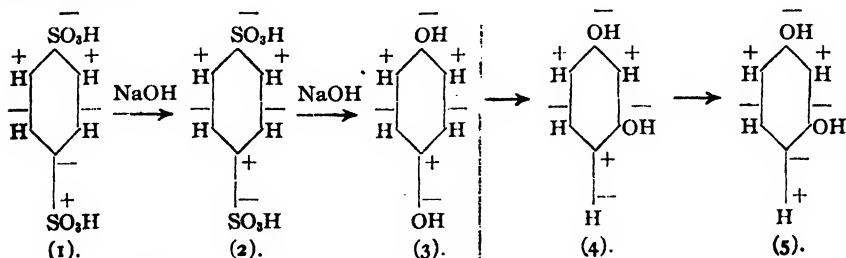
"According to Fry, 'the radical SO_2H in phenylsulfonic acid may function either positively or negatively.' He deduces this from the fact that this acid yields benzene on heating with water or acids, but phenol on melting with alkali. But since in *o*- and *p*-phenylene disulfonic acid one SO_2H should be positive when the other is negative, these acids should yield phenol exclusively on melting with alkali. In reality they yield pyrocatechol and hydroquinol."

In reply this objection is apparently justified but it is invalidated by Holleman's failure to take into account the fact that whether the SO_2H radical be positive or negative, in alkaline solution it functions negatively. For instance, since phenylsulfonic acid is a mixture of tautomeric electromers ($\overset{+}{\text{C}_6\text{H}_5}\text{SO}_2\text{H} \rightleftharpoons \overset{-}{\text{C}_6\text{H}_5}\text{SO}_2\text{H}$), the former would revert to the latter in acid solution, but in alkaline solution the latter reverts to the

former, *i. e.*, SO_3H becomes SO_3H^- and is replaced by OH^- on hydrolysis. Applying this principle to *o*- or to *p*-phenylene disulfonic acid, each containing (SO_3H^+) and (SO_3H^-) , fusion with alkali would cause both radicals to function negatively with consequent replacement by negative hydroxyl yielding pyrocatechol and hydroquinol:



At once it will be contended that these electronic formulas are exceptional since the general rule has consistently maintained that substituents ortho and para to each other are of opposite polarity. Granting the above formulas to be exceptions we are presented with evidence that substantiates a fundamental principle, namely, that if the polarities of the hydrogen atoms or substituents of the nucleus do not conform to the general electronic formula for benzene, then the stability of the benzene nucleus is radically affected. Now this ensuing instability actually manifests itself in the fact that *o*-, *m*-, and *p*-bromobenzenesulfonic acids, and *m*- and *p*-phenylene disulfonic acids, all yield one and the same dihydric phenol—namely, the *meta* compound, resorcinol, on fusion with potassium hydroxide. Perkin and Kipping,¹ commenting upon these anomalies state that the ortho and para dihydric compounds which are first produced from the corresponding bromosulfonic acids (or from the corresponding phenylene disulfonic acids) are unstable and are converted into the more stable *meta*-derivative by intramolecular change. Now the electronic hypothesis readily furnishes an interpretation of this instability as due to the disarrangement of the electronic symmetry of the electrical charges when radicals ortho or para to each other are of the same sign. For instance, all of the changes involved in the conversion of *p*-phenylenedisulfonic acid to resorcin are illustrated in the following electronic formulas and scheme:



¹ "Organic Chemistry," pp. 436-7 (1911).

Formula 1 is the natural symmetrical *p*-disulfonic acid. In alkaline medium SO_3H becomes SO_3H^- , *i. e.*, the negative valence of C-atom 4 is converted to a positive valence (by the loss of two electrons which render SO_3H negative) and the resulting Formula 2 is not symmetrical. Hydrolysis yields the nonsymmetrical and unstable dihydric phenol of Formula 3 which undergoes intramolecular rearrangement. This rearrangement may be attributed to two tendencies: first, $\text{OH}^- > \text{H}^+$, and second, $\text{H}^+ > \text{H}^-$. The first is fulfilled when OH^- occupies position 3 meta to OH^- in position 1. The second leads to the change in the polarity of carbon valence 4, H^- becoming H^+ (as in Formula 5) which completes the transition to the symmetrical and stable resorcin.

(4) In the fourth paragraph, Holleman indicates the electronic formulas of *p*-chlorotoluene and *p*-chlorobromobenzene and maintains that if Fry's rule were correct we should obtain, on nitration, only one nitrochlorotoluene and only one nitrochlorobromobenzene; when, as a matter of fact, Wibaut and Heineken proved that in both cases, considerable quantities of two isomers are obtained. In reply, this objection is invalidated because Holleman failed to take into account the two electromers (electronic tautomers) of each of these para compounds. A detailed explanation of the introduction of a third substituent Z ($= \text{NO}_2$) into a paradisubstituted derivative, $\text{C}_6\text{H}_4\text{XY}$ ($\text{X} = \text{Cl}$; $\text{Y} = \text{CH}_3$ or Br) is given in detail in Part IV, Section B, Scheme 2, which shows that the researches of Wibaut (as quoted by Holleman) actually confirm the electronic tautomerism of the derivatives and rule for substitution.

Again, Holleman states that the nitration of *o*-chlorotoluene yields, as shown by Wibaut, all four possible isomers of nitrochlorotoluene, while Fry's rule predicts the formation of only two isomers. In reply, Holleman again fails to consider the part played by both tautomeric electromers of *o*-chlorotoluene on nitration. In Part IV, Section B, Scheme 1, I have shown that the introduction of a third substituent into an ortho-disubstituted derivative yields *four* possible isomers. The work of Wibaut, discussed in this section, affords a striking confirmation of the electronic tautomerism of *o*-chlorotoluene and the electronic scheme for its nitration.

The fact that Holleman obtains only two isomers when *o*-chlorobromobenzene is nitrated accords with the fact that only one of the electromers enters into reaction with nitric acid. This is perfectly analogous to the nitration of monochlorobenzene in which only one electromer enters into reaction with consequent formation of only two isomers.

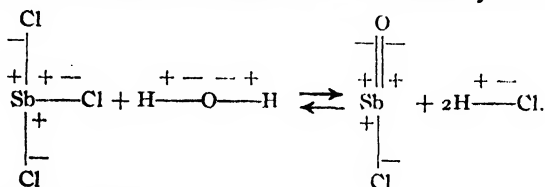
In concluding this part of the reply, each of the objections cited by Holleman in the fourth paragraph of his criticism, accords with and, therefore,

substantiates the electronic formulas, the schemes of electronic tautomerism and the rule for substitution as resented in Part IV, Section B.

(5) In his fifth paragraph Holleman states:

"Fry's explanation of the fact that the chlorination of nitrobenzene yields *m*-nitrochlorobenzene, can neither be accepted. He supposes that $\text{HO} \cdot \text{Cl}$ is the chlorinating agent 'since absolutely anhydrous chlorine does not react with anhydrous reagents.' However, this introduction of chlorine is only possible, when a large quantity of SbCl_3 is added ($1/5$ of the weight of the nitrobenzene). All traces of water must be taken away by it."

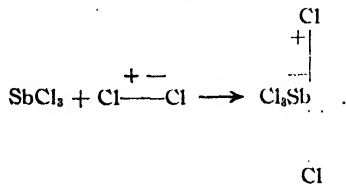
In reply, it cannot be asserted absolutely that all traces of water are removed by SbCl_3 because its interaction with water is a decidedly reversible reaction which may be represented electronically as follows:



Holleman then continues:

"The only plausible explanation is, that SbCl_5 is formed which transports chlorine to the nitrobenzene. As there can be little doubt that SbCl_5 is SbCl_3 (always according to the views of Fry), chlorine ought to replace an *o*- or *p*-H-atom in $\text{C}_6\text{H}_5\text{NO}_2$, when NO_2 in it is positive."

In reply to this statement, I am perfectly willing to admit that SbCl_3 may act as a halogen carrier through the intermediate formation of SbCl_5 , but I have never claimed (as attributed to me by Holleman) that SbCl_5 is SbCl_3 , which as an electronic formula is meaningless. The electronic formula for SbCl_3 is given in the hydrolysis equation above, and its combination with chlorine to act as a halogen carrier is as follows:



Now, in Part II of this series, *THIS JOURNAL*, 36, on page 1042, I have given an explanation and scheme for the action of halogen carriers in effecting the nucleus substitution of *positive halogen*. The action of SbCl_5 as a halogen carrier conforms perfectly with this explanation and scheme for the nucleus substitution of positive chlorine which must assume a position meta to the positive nitro radical in nitrobenzene. See the complete electronic scheme for the formation of a meta-disubstituted de-

rivative in Part IV, Section D, which also shows that positive chlorine must replace a meta-hydrogen atom in $\text{C}_6\text{H}_5.\text{NO}_2$ and not an ortho or para hydrogen atom as incorrectly attributed to my hypothesis by Holleman.

(6) In the sixth paragraph, Holleman, admitting Fry's explanation of the replacement of negative chlorine in *o*- and *p*-chloronitrobenzenes by negative hydroxyl, and the nonreplacement of positive chlorine in *m*-chloronitrobenzene, states:

"One chlorine should also be replaceable by OCH_3 in *o*- and *p*-dichlorobenzene, $\text{Cl}.\text{C}_6\text{H}_4.\text{Cl}$, but not in *m*-dichlorobenzene, $\text{Cl}.\text{C}_6\text{H}_4.\text{Cl}$ (or $\text{Cl}.\text{C}_6\text{H}_4.\text{Cl}$). However, deMooy (work not yet published) has proved in my laboratory, that the latter also reacts with sodium methylate, and that the velocity of this reaction is even greater than for the para and ortho isomers, one Cl-atom being replaced in all three compounds."

In reply, this is just what the electronic hypothesis would naturally predict, for if *m*-dichlorobenzene is a mixture of the electronic tautomers, $\text{Cl}.\text{C}_6\text{H}_5.\text{Cl} \rightleftharpoons \text{Cl}.\text{C}_6\text{H}_5.\text{Cl}$, then the former electromer in which chlorine is negative would naturally predominate (since $\text{Cl}^- > \text{Cl}^+$) and lend itself to interaction with $\text{Na}.\text{OCH}_3$ according to the equation:



Furthermore, I have shown in Part IV, Section B, under Scheme 3, that in a meta-disubstituted derivative, if both substituents tend to function negatively rather than positively (as is the case in *m*-dichlorobenzene) then that electromer will tend to predominate to the exclusion of the other electromer. Hence, the predominance or increased concentration of the electromer $\text{Cl}.\text{C}_6\text{H}_4.\text{Cl}$ explains its greater speed of interaction with $\text{Na}.\text{OCH}_3$. An analogy is afforded in the greater speed of interaction between $\text{C}_6\text{H}_5.\text{Cl}$ and nitric acid than between $\text{C}_6\text{H}_5.\text{Cl}$ and nitric acid, previously considered. Accordingly the velocity of reaction between $\text{Cl}.\text{C}_6\text{H}_4.\text{Cl}$ and sodium methylate would be greater than the velocity of reaction between $\text{Cl}.\text{C}_6\text{H}_4.\text{Cl}$ (*o* or *p*) and sodium methylate.

Thus the experimental facts presented by Holleman in his sixth paragraph of objections are found to be in harmony with the electronic principles previously developed and applied.

In his concluding paragraph, Holleman states:

"I wish, finally, to call attention to two further points. In the first place, it would probably be very difficult to designate what charge a given substituent has. In most cases it might as well be positive as negative. This naturally leads to a great uncertainty in the explanation of reactions."

In reply, it may be admitted that difficulties are sometimes encountered in determining the charge of a given substituent, but this is not always so. For instance, W. A. Noyes, Stieglitz, L. W. Jones, Falk and Nelson, Bray and Branch, and others, have made extended and highly significant applications¹ of the electronic conception of positive and negative valences, and have demonstrated that the reactions of hydrolysis may be employed frequently to determine the polarity or charge of certain radicals. Furthermore, in Part III of this series, in the further analysis of the Brown and Gibson rule, I have shown that those various substituents which lead to the formation of ortho- and para-derivatives do so by virtue of their *negative polarity*, while those various substituents which lead to the formation of meta-derivatives do so by virtue of their *positive polarity*. In other words, the *ortho-para* and *meta* types of substitution in the benzene nucleus afford a key to the determinations of the polarities of numerous substituents.

While it is true that a given substituent may function either positively or negatively, I have shown that said substituent possesses a definite and a pronounced tendency to function in one way rather than in another way. This fact has been of great importance to the conception of electronic tautomerism and the explanation of (1) the simultaneous formation of ortho-, meta- and para-derivatives, (2) the velocities of substitution reactions, and (3) the relative yields of the possible isomers. Further confirmations of these principles are reserved for subsequent papers. Hence, we may conclude that the determination of the polarity of a substituent is neither so difficult nor as uncertain as some might be inclined to judge. Further developments of the electronic conception of positive and negative valences are certain to throw more light upon this phase of the subject.

Finally, Holleman states:

"In the second place, I might direct attention on the consequences of the hypothesis in the case of open chains. For these it leads to the formula

$$\overset{+}{\text{C}}_1 - \overset{-}{\text{C}}_2 - \overset{+}{\text{C}}_3 - \overset{-}{\text{C}}_4 - \overset{+}{\text{C}}_5 - \overset{-}{\text{C}}_6,$$

for the linking of the C-atoms comes about by C-atom 1 giving off an electron to C-atom 2, this sending off an electron in its turn to C-atom 3, and so on. This must cause the C-atoms at both ends of the open chain to have opposite signs. This would involve the consequence that the Br-atoms, *e. g.*, in a polymethylene dibromide, ought to show a different behavior, which is also in contradiction with the experimental facts."

In reply, this final objection of Holleman is itself subject to criticism because his assumption relative to the electronic nature of the open carbon chain is arbitrarily limited to only one type of linking. It is equally possible to have carbon chains of several types. For example, the following type would accommodate halogen atoms of the same polarity at each

¹ See references to the articles of these authors throughout the present series of papers.

end of the chain: $\overset{+}{\text{C}}-\overset{+}{\text{C}}-\overset{-}{\text{C}}-\overset{-}{\text{C}}-\overset{+}{\text{C}}-\overset{+}{\text{C}}-\overset{-}{\text{C}}-\overset{-}{\text{C}}-\overset{+}{\text{C}}-\overset{+}{\text{C}}$. I shall also show in a later paper that halogen atoms at the ends of an open carbon chain are of opposite polarity just as are the halogen atoms on carbon atoms 1 and 4 of the benzene nucleus in *p*-dichlorobenzene.

In conclusion, it may be said that criticisms of a hypothesis should be and are welcomed because they serve to develop either its merits or demerits. The electronic hypothesis of positive and negative valences, while comparatively new, is a rapidly growing conception as is evidenced by the articles of the authors noted above who have presented many significant applications, interpretations, and deductions. The present series of papers relating chiefly to the constitution of benzene and its derivatives, has interpreted many hitherto unexplained phenomena. The fact that electronic formulas, in many instances, have proven to be of greater significance than the ordinary structural formulas lends support to the idea that the electronic conception of positive and negative valences may become not only a significant but possibly a necessary adjunct to the structure theory. This however, must depend upon the extent of its applications and experimental verifications, and upon the part that is played by just criticisms in bringing to light the relative merits and demerits of its applications.

CINCINNATI, O.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SYRACUSE UNIVERSITY.]
**A METHOD FOR THE SEPARATION AND IDENTIFICATION OF
 CERTAIN HOMOLOGOUS α -DIKETONES.**

By J. M. JOHLIN.

Received January 25, 1915.

The author has made the observation that diacetyl occurs in considerable quantities in pyroligneous acid, and generally in smaller amounts in the distillate resulting from the destructive distillation of carbohydrates, such as pure cellulose, cane sugar, glucose, and lactose.

The fact that nickel readily precipitates as the salt of dimethylglyoxime was adapted for the precipitation of diacetyl with nickel chloride and hydroxylamine-hydrochloride. Repeated preliminary tests with synthetically prepared diacetyl showed that one part of diacetyl in one hundred thousand parts of water still gives a decided precipitate of the nickel salt of dimethylglyoxime when a few drops each of solutions of nickel chloride, hydroxylamine-hydrochloride and ammonium hydroxide are added. Although diacetyl itself is very volatile it is evident that, after adding the reagent necessary for its precipitation, concentration to any necessary extent can be effected without further loss.

Dimethylglyoxime, which can be prepared in a very pure state and accurately weighed, was found by repeated determinations to be quanti-

tatively precipitated from solution when the proper amounts of sodium acetate, nickel chloride and ammonium hydroxide were added.

| | Wt. of dioxime taken. G. | Wt. of nickel salt precipitated. G. | Wt. of dioxime found. G. | Loss. %. |
|--------|-----------------------------|--|-----------------------------|-------------|
| 1..... | 0.1012 | 0.1259 | 0.1012 | 0.00 |
| 2..... | 0.1001 | 0.1244 | 0.1000 | 0.10 |
| 3..... | 0.1003 | 0.1243 | 0.0999 | 0.39 |

Since the nickel salt of dimethylglyoxime is practically insoluble in water, it should be possible to precipitate any of its three components quantitatively, using the other two as reagents. As diacetyl always occurs in acid solution, and since hydrochloric acid is one of the products of the reaction when it is precipitated in the form of the nickel salt of its dioxime, an exactly neutral solution is difficult to obtain. The solubility of the nickel salt in acid solution depends upon its dissociation into the nickel salt of the acid present and into dimethylglyoxime. This dissociation is less with acetic acid than with any of the mineral acids. Sodium acetate then not only sets free acetic acid in place of hydrochloric, but also furnishes a common acetate ion. That the addition of sodium acetate lessens the solubility of the nickel salt of the dioxime in dilute acetic acid solutions was shown experimentally. Though the amount of nickel salt dissolved by a solution of one part of acetic acid in fifty thousand parts of water is small, it is sufficiently large to be visibly reprecipitated when minute quantities of sodium acetate are added. Ammonium hydroxide when carefully added is more effective than sodium acetate in aiding complete precipitation. An excess of ammonium hydroxide must be avoided since it also dissolves small amounts of the nickel salt of the dioxime. The presence of ammonium chloride is necessary to prevent the precipitation of nickel hydroxide.

This method applied to the quantitative determination of diacetyl in pyrolygneous acid gave results which made it evident that other homologous diketones were present, thus giving rise to the necessity of a qualitative scheme for their separation and identification.

The possibility of identifying these diketones occurring in so small amounts in the presence of each other depends upon a detailed knowledge of the properties of their dioximes and of the nickel salts of these.

The dioxime of diacetyl, that of its higher homolog acetylpropionyl, and that of its lower homolog methylglyoxal, a keto-aldehyde, were prepared according to the method of Diels¹ and Jost as modified by Gandarin² for the preparation of dimethylglyoxime. In each case the proportionate amounts of methyl ethylketone, of diethylketone, and of acetone were oxidized with iso-amyl nitrite to the isonitroso compound and after

¹ *Ber.*, 35, 3290 (1902).

² *J. prakt. Chem.*, 77, 414 (1908).

adding hydroxylamine hydrochloride extracted with ether in the form of the dioximes. From the dioximes their respective nickel salts were prepared.

All three dioximes readily sublime when heated and can, by resubliming, be separated from other nonvolatile matter. According to their solubility in hot and cold water the two higher homologs can readily be freed from the lowest by recrystallizing them from water.

The nickel salt¹ of dimethylglyoxime is practically insoluble in both hot and cold water. That of the higher homolog is very sparingly soluble even in hot water. That of the lower homolog is slightly soluble in cold water and sufficiently soluble in hot water to make possible its recrystallization from large amounts of this solvent.

Dilute ammonium hydroxide very readily dissolves the nickel salt of the lowest homolog, while the nickel salt of dimethylglyoxime is but sparingly soluble even in stronger solutions of ammonia. Ether which has been thoroughly dried dissolves the nickel salt of methylethylglyoxime, while that of dimethylglyoxime is practically insoluble and that of methylglyoxime but sparingly soluble in the same solvent.

The insolubility of the nickel salts of the dioximes of the diketones in neutral solutions, then, makes it possible to precipitate them completely even where they occur in minute quantities. The physical properties of the nickel salts and of the free dioximes give further evidence that it is possible to separate them from each other, to recover the free dioxime from each salt individually, to purify it, and by means of its melting point to identify the diketone of which it is a derivative.

A known mixture containing 0.1 g. each of nickel methylglyoxime, of nickel dimethylglyoxime, and of nickel methylethylglyoxime was used to test the efficiency of such an analysis. The amounts of these nickel salts taken represent, respectively, 0.056 g. of methylglyoxal, 0.061 g. of diacetyl, and 0.064 g. of acetylpropionyl.

The mixture was first subjected to an extraction with ether dried over sodium. It required but two extractions with 200 cc. of dried ether to completely remove all of the nickel salt of methylethylglyoxime, along with traces of the nickel salt of methylglyoxime. The ether extract was concentrated to about 50 cc. and then thoroughly shaken with an equal volume of 5% sulfuric acid until the yellow color of the ether extract and precipitated nickel salt had entirely disappeared. The ether layer now contained all of the methylethylglyoxime and traces of methylglyoxime, while the acid layer contained all of the nickel in the form of its sulfate. After separating the two layers the ether was evaporated and the methyl-

¹ Sufficient detail regarding the physical properties of these nickel salts is in some instances not supplied by Tschugaeff. In other instances, where the Russian literature was not available, abstracts of the original articles were too brief to mention physical properties at all.

MIXTURE CONTAINS THE NICKEL SALTS OF

Methylglyoxime.

Dimethylglyoxime.

Methylmethylglyoxime.

Extract with ether

Ether extract contains
nickel salt of methylmethylglyoxime,
traces of nickel salt of methylglyoxime

↓
Ether extract is shaken with 5% H_2SO_4 .

Ether layer contains
methylmethylglyoxime
traces of methylglyoxime

Acid layer contains
nickel sulfate

↓
Evaporate ether and
recrystallize residue
from water

Recrystallized oxime is
pure methylmethylglyoxime,
melts at 171° , identifies
acetylpropionyl

Residue contains
nickel salts of methylglyoxime,
and of dimethylglyoxime

↓
Extract with dilute ammonia

Extract contains
nickel salt of methylglyoxime,
traces of nickel salt of
dimethylglyoxime

↓
Acidify with 5% H_2SO_4 ,
and extract with ether

Ether layer contains
methylglyoxime,
traces of dimethyl-
glyoxime

Acid layer
contains
 $NiSO_4$ and
 $(NH_4)_2SO_4$

↓
Evaporate ether
and dissolve residue
in water
Precipitate dimethylglyoxime
completely with $NiCl_2$ and filter

Filtrate contains
methylglyoxime

Ppt. contains
traces of nickel salts
of dimethylglyoxime
and of methylglyoxime

↓
Acidify, extract with
ether, evaporate ether,
and resublime oxime

↓
Resublimed oxime is pure methylglyoxime,
melts at $155-156^\circ$, identifies methylglyoxal

Residue contains
nickel salt of dimethylglyoxime] Shake with ether and 5% H_2SO_4 ,
↓

Ether layer contains
dimethylglyoxime

Acid layer
contains
 $NiSO_4$

↓
Recrystallize from water

Recrystallized oxime is
pure dimethylglyoxime, melts
at $234-235^\circ$, identifies
diacetyl

ethylglyoxime purified by recrystallization from a small amount of water. The material thus recovered was found to melt¹ sharply at 171.°

The residue of nickel salts left by the ether extraction was now thoroughly shaken with dilute ammonium hydroxide. After filtering, the filtrate was acidified with dilute sulfuric acid to a point where any precipitated nickel salt of methylglyoxime redissolved and the solution instead of having a golden yellow color had become colorless. The mixture was now extracted with ether. The methylglyoxime obtained from the ether extract was freed from traces of dimethylglyoxime by redissolving both in water containing a few drops of dilute ammonium hydroxide and adding to this solution a few drops of very dilute nickel chloride. Since the nickel salt of dimethylglyoxime is practically insoluble in so dilute a solution of ammonia, traces of it would thus be precipitated and can be removed by filtration. This procedure was continued until there was sufficient indication that all of the dimethylglyoxime had been removed. The complete removal of dimethylglyoxime is shown by the appearance of the precipitation of the scarlet modification of the nickel salt of methylglyoxime which readily changes over into the more stable yellow modification, and further by the appearance of a yellowish solution due to the solubility of nickel methylglyoxime in ammonia solutions. The solution was again made just acid with dilute sulfuric acid and the methylglyoxime extracted with ether and resublimed. The resublimed dioxime thus recovered melted¹ at 155-156°.

The residue containing the nickel salt of dimethylglyoxime left by the ammonia extraction was thoroughly shaken with 50 cc. of 5% sulfuric acid and an equal volume of ether. The ether layer containing the free dioxime was evaporated and the dioxime recrystallized from water. The substance thus recovered and purified was found to melt¹ at 234-235°.

The accompanying diagram graphically outlines the course of the analysis which isolates from a mixture containing minute quantities of the insoluble nickel salts of the dioximes of these α -diketones, the pure dioximes whose melting point identifies each homolog.

THE SEPARATION OF ETHANE AND ETHYLENE BY FRACTIONAL DISTILLATION IN A VACUUM AT LOW TEMPERATURES.²

By G. A. BURRELL AND I. W. ROBERTSON.

Received February 15, 1915.

This paper shows some experiments made by the authors, at the Pittsburgh Experiment Station of the Bureau of Mines, in separating ethane and ethylene by fractional distillation in a vacuum at low temperatures. In previous communications there was shown the separation of gases

¹ Cf. Glyoxime, Beilstein, *Organische Chemie*.

² Published by permission of the Director of the Bureau of Mines.

whose boiling points are wide apart: (1) the separation of the constituents in natural gas,¹ and (2) the separation of the illuminants in artificial gas.² Some of the constituents of the latter were separated in pairs, *i. e.*, ethane, b. p. -93° , and ethylene, b. p. -103° , were separated together, as were propane, b. p. -45° , and propylene, b. p. -51° . They were finally analyzed together by burning them in oxygen. From the carbon dioxide and contraction produced, the percentage of each was calculated.

It was desirable to learn something of the limitations of this method of separating gases; for instance, just how tedious would be the work involved in separating the gases ethane and ethylene, whose boiling points are only 10° apart, when the percentage of each present was large.

Experimental.

Preparation of Ethane.—Ethane was prepared by the electrolysis of a saturated solution of sodium acetate. The carbon dioxide evolved with the ethane was removed with caustic potash. Air or other gases trapped with the ethane were removed by fractional distillation in a vacuum at temperatures ranging from that of liquid air to -120° .

Preparation of Ethylene.—Ethylene was prepared by heating ethyl alcohol and sulfuric acid together at a temperature of 160° . The evolved gases were purified in the same way as the ethane. The purity of the two gases was determined by combustion analysis.

Vapor Pressures of Ethane and Ethylene.—It was first necessary to determine temperatures at which the separation could be effected, *i. e.*, temperatures at which the vapor pressure of ethane is practically nil and that of ethylene high enough so that the latter could be withdrawn from the mixture, finally leaving all of the ethane behind. It was found that ethane has a vapor pressure at 160° of 1 mm. of mercury, while that of ethylene at the same temperature is 4 mm. At -170° the vapor pressure of ethylene was found to be 1 mm., while the manometer did not register any pressure for ethane. These pressures are accurate to 1 mm. at the lower temperature.³ Temperature readings were made with a pentane thermometer. A wide variation in temperature represented only a small pressure change at the lowest temperatures. The foregoing vapor pressures showed that the separation could probably be accomplished at temperatures of -170° or slightly higher.

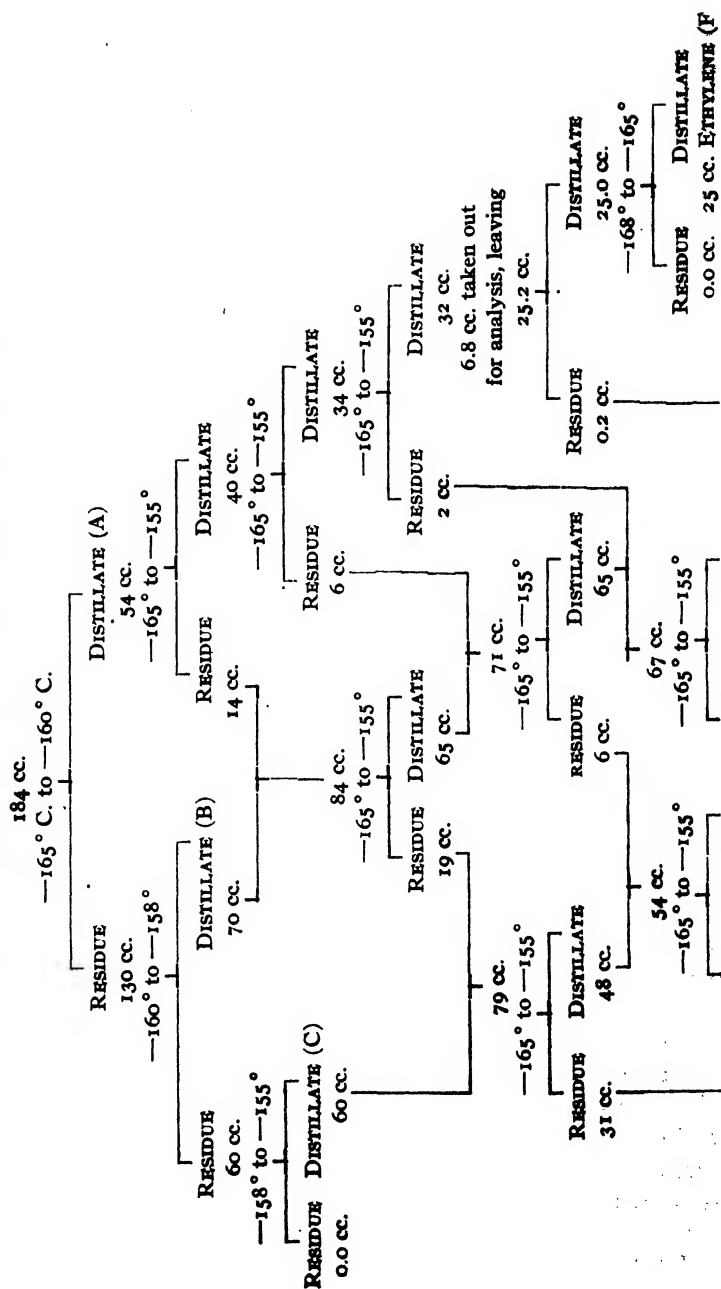
Separation of the Gases.—The two gases were mixed in equal proportions, 92 cc. of ethane and 92 cc. of ethylene. The fractionation was first tried at temperatures close to -170° , but so much ethylene was present, its removal so slow, and so much difficulty was experienced in maintaining a constant temperature for a long time, that higher temperatures and a

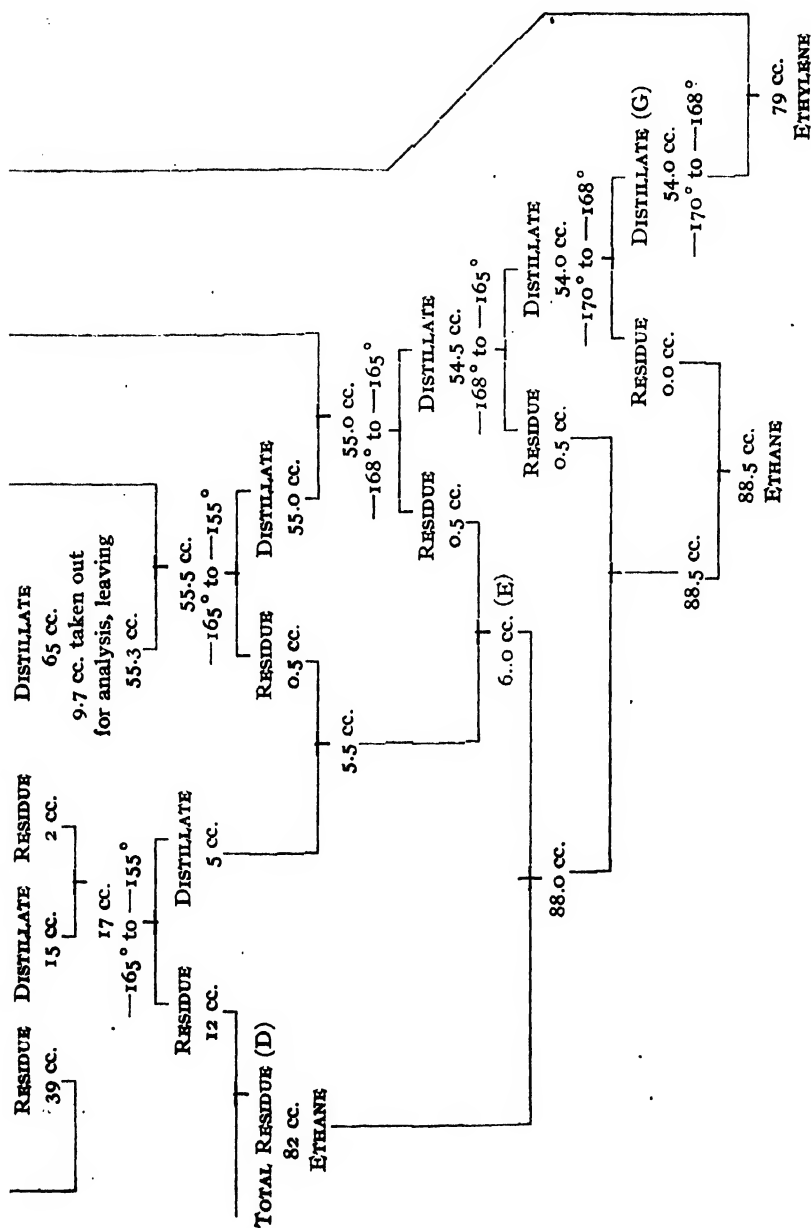
¹ THIS JOURNAL, 36, 1537 (1914); 37, 392 (1915).

² J. Ind. Eng. Chem., 7, 17-21 (1915).

³ These vapor pressure measurements will be given in a subsequent paper.

FIGURE I.—FRACTIONAL DISTILLATION OF ETHYLENE AND ETHANE





wider range was employed to first make an approximate separation. Hence the first fractionations were made at -160° to -155° , the second at -165° to -155° , the third at -168° to -165° , and the last ones at -170° to -168° .

At -165° to -160° .—There was obtained a distillate of 54 cc. This is marked distillate A on the diagram, Fig. 1. The residue from this distillation was refractionated at -160° to -158° . There was obtained 70 cc. of distillate (distillate B). The residue from this second distillation was refractionated at -158° to -155° and there was obtained 60 cc. of distillate (distillate C). No residue was left. It should be stated that at any of these temperatures all of the gas could be removed as a distillate in a comparatively short time by continuing the pumping long enough. The object was simply to divide the original portion into several fractions, each containing considerably more of one constituent than another, so that an excessive amount of gas would not have to be removed at lower temperatures, where the distillation proceeds more slowly.

Second Series of Fractionations.—The first distillate of 54 cc. (A) was refractionated at temperatures ranging from -165° to -155° . A distillate of 40 cc. was obtained. To the residue of 14 cc. there was added distillate B (70 cc.). This total (84 cc.) was distilled at -165° to -155° . The distillate amounted to 65 cc. and the residue to 19 cc. To the latter there was added distillate C (60 cc.). This total (79 cc.) was distilled at temperatures ranging from -165° to -155° . The distillate amounted to 45 cc. and the residue to 31 cc.

The foregoing illustrates the general procedure. All told, 18 fractionations were made. The diagram, Fig. 1, shows the various steps.

There was finally obtained 88.5 cc. of ethane and 79 cc. of ethylene. Two portions, one of 6.8 cc. and one of 9.7 cc. (total 16.5 cc.) had been removed during the fractionation as noted on the diagram, in order to determine by combustion analysis the purity of the fractions. In each case the separation was found to be incomplete. When this portion (16.5 cc.) is added to the final ethane and ethylene total (88.5 + 79 cc.) there results 184.0 cc., a quantity equal to the original amount.

Purity of the Fractions.—There are given below analyses of the various fractions to show their purity. They were examined by burning them with oxygen. The percentage of each constituent was calculated from the contraction and carbon dioxide produced.

According to the reaction, $\text{C}_2\text{H}_6 + 3.5\text{O}_2 = 2\text{CO}_2 + 3\text{H}_2\text{O}$, there result two volumes of CO_2 and a contraction of 2.5 volumes when ethane reacts with oxygen. It will be noted that the observed data correspond well with the theoretical equation.

TABLE I.

Analysis of Ethane.—Three of the following analyses were made of the residue marked *D* in the diagram. The total quantity of gas collected at this point was 82 cc. Three analyses were made. The data show analysis of ethane fraction.

The analysis in last column was made of the distillate marked (E) on the diagram (6 cc.):

| Analysis No. | 1. Cc. | 2. Cc. | 3. Cc. | 4. Cc. |
|--|-----------|-----------|-----------|-----------|
| Gas taken for analysis..... | 9.00 | 20.23 | 21.03 | 6.00 |
| Oxygen added..... | 63.47 | 83.37 | 97.82 | 75.43 |
| Total volume..... | 72.47 | 103.60 | 118.85 | 81.43 |
| Volume after burning..... | 49.84 | 53.22 | 66.57 | 66.43 |
| Contraction..... | 22.63 | 50.38 | 52.28 | 15.00 |
| Volume after CO ₂ absorption..... | 31.77 | 12.81 | 24.45 | 54.71 |
| CO ₂ produced..... | 18.07 | 40.41 | 42.12 | 11.72 |
| Ethane calculated from contraction..... | 9.05 | 20.15 | 20.91 | 6.00 |
| Ethane calculated from CO ₂ | 9.04 | 20.20 | 21.06 | 5.88 |

TABLE II.

ANALYSES OF THE ETHYLENE FRACTIONS.

Two of the following analyses were made of the ethylene distillate marked (F) on the diagram (25 cc. of distillate) and one of the distillate marked (G):

| Analysis No. | 1. Cc. | 2. Cc. | Analysis of distillate G. Cc. |
|--|-----------|-----------|-------------------------------------|
| Sample taken..... | 9.00 | 9.20 | 19.55 |
| Oxygen added..... | 47.10 | 43.76 | 73.25 |
| Total volume..... | 56.10 | 52.96 | 92.80 |
| Volume after burning..... | 38.45 | 34.87 | 53.81 |
| Contraction..... | 17.65 | 18.09 | 38.92 |
| Volume after CO ₂ absorption..... | 20.70 | 16.70 | 14.82 |
| CO ₂ | 17.75 | 18.17 | 38.99 |
| Ethylene calculated from the contraction..... | 8.83 | 9.05 | 19.46 |
| Ethylene calculated from the CO ₂ | 8.87 | 9.08 | 19.50 |

According to the reaction $\text{C}_2\text{H}_4 + 3\text{O}_2 = 2\text{CO}_2 + 2\text{H}_2\text{O}$, there result 2 volumes of carbon dioxide and a contraction of 2 volumes when ethylene reacts with oxygen. The carbon dioxide and contraction in the foregoing analyses correspond with this reaction. In the case of analysis No. 1 the ethylene was not 100% pure, however, probably due to the intrusion of a trace of air. This point was not tested.

Conclusions.

Although the foregoing separation is complete within the error of making the analyses, the work involved is too tedious to be entirely satisfactory when the proportions of each constituent are present in considerable quantity. The ease of separation of gases whose boiling points are widely separated¹ is in sharp contrast to the separation recorded in this paper.

Constant temperatures were too difficult to maintain, and the removal of the gas by the pump too irregular at any particular temperature to

¹ *Loc. cit.*

obtain a ratio between the quantity of gases removed at different temperatures. As is invariably the case with liquids that tend to separate into two components, the less volatile one of the two (the ethane) was easier to obtain in a pure state. It is intended to repeat the work with a smaller percentage of one of the gases present than of the other and with the use of a thermostat such as was devised by F. Henning.¹ In another communication will also be shown the application of this method of separation to substances that are liquids at ordinary temperatures. In some separations the advantages over the use of high temperatures are: (1) The elimination of complicated still heads, and (2) the avoidance of loss by evaporation because high temperatures are not used. A different means of trapping the liquid had to be devised than that used in handling liquid gases.

All temperatures are in degrees centigrade. Details of the apparatus used are given in previous communications.

PITTSBURGH, PA.

[FROM THE CHEMICAL LABORATORY OF THE COLORADO AGRICULTURAL COLLEGE.]

ON THE OXIDATION OF ETHER.

BY R. M. ISHAM AND C. E. VAIL.

Received February 5, 1915.

It seems somewhat surprising to the authors that the subject of the oxidation of ether should have received but slight attention from the writers of our texts on organic chemistry. While the behavior of the alcohols and aldehydes on oxidation is considered in some detail, as representing important type reactions of these substances, the majority of our texts have nothing at all to say regarding the behavior of the closely related ethers. This is the more remarkable in consideration of the fact, which we shall show, that ether is very readily oxidized to aldehyde and acetic acid.

In the third American edition of Richter's "Organic Chemistry," Vol. I, p. 133, we find the statement that "When oxidized they (the ethers) yield the same products as their alcohols." Stoddard's "Introduction to Organic Chemistry," p. 73, states that "Oxidation (of ether) by means of nitric or chromic acid produces the same products as those obtained by the oxidation of alcohol—aldehyde and acetic acid." On the other hand, the 1907 edition of Roscoe and Schorlemmer's "Treatise on Chemistry," Vol. II, p. 1002, states that "Chromium trioxide dissolves without alteration in pure ether," a statement which we were by no means able to verify. Aside from the above we have not, in a neces-

¹ *Z. Instrumentenkunde*, 33, 33 (1913). This thermostat was installed by the authors just before this article went to press. With it temperatures can be controlled within 0.03°.

sarily somewhat incomplete survey of the texts, found any reference to this subject.

Löw¹ has shown that ether vapor, when mixed with air and passed over a heated superficially oxidized copper spiral, is oxidized to aldehyde.

W. H. Perkin² found that when ether vapor mixed with oxygen, in a quantity insufficient to produce total oxidation, was passed through a tube heated to temperatures between 260° and dull redness, a pale luminous flame resulted, and the ether was oxidized, chiefly to aldehyde. Similarly, Dunstan and Dymond³ found the incomplete *combustion* of ether to give aldehyde and acetic acid as chief products.

Richardson and Forty⁴ obtained evidence of a photochemical oxidation to aldehyde and acetic acid, on exposing a vessel containing ether and oxygen, in contact with water, to direct sunlight for a period of five weeks.

Aside from the above we have been able to find no reference to the direct oxidation of ether by means of air or oxygen.

We have been able to show that ether vapor is readily oxidized to aldehyde and acetic acid, when mixed with air or oxygen, without the use of any catalyst and at temperatures very much below that at which luminous combustion begins.

The attention of one of us was first directed to this subject when a strong odor of acetaldehyde was noted issuing from a Freas electric oven, in which the residues from the ether extraction of some wheat samples were being dried at a temperature of 110°. The natural inference that the aldehyde resulted from the oxidation of ether was shown to be correct by saturating some filter papers with ether and placing them in the oven, when, after heating for some time at 110°, a strong odor of aldehyde was noted on opening the oven. Since the literature on this subject seemed to be somewhat incomplete we were lead to carry out some further experiments.

A three-holed Woulff bottle of 750 cc. capacity was fitted with an inlet tube extending to the bottom of the bottle, an exit tube extending only through the stopper, and a thermometer, and the whole placed in an air bath.

In a preliminary experiment a side-neck test tube, containing 10 cc. of pure ether, and provided with an inlet tube for oxygen, extending to the bottom, was connected to the inlet tube of the Woulff bottle, and a Liebig condenser attached to its exit tube. The temperature of the Woulff bottle was brought to 120°, while the temperature of the ether was maintained at 12° ± 1, at which temperature, and at our normal barometric

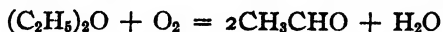
¹ *J. prakt. Chem.*, 141, 323.

² *J. Chem. Soc.*, 41, 363 (1882).

³ *Ibid.*, 57, 574 (1890).

⁴ *Ibid.*, 69, 1352 (1896).

pressure (ca. 635 mm.), a mixture of its saturated vapor with oxygen should be nearly equimolecular, as required for the equation:



Oxygen was bubbled through the ether at such a rate that evaporation was complete in a little less than two hours, so that the mixed gases were exposed to the elevated temperature of the Woulff bottle for an average period of about ten minutes. A very strong odor of aldehyde was apparent in the vapors issuing from the condenser, and a couple of drops of the condensed product, which consisted largely of ether, immediately restored the color to a little Schiff fuchsin-aldehyde reagent.

The formation of aldehyde having thus been proven, it was decided to so modify our apparatus as to permit of quantitative experiments. For this purpose, the condenser was replaced by a thistle-tube, connected to the exit tube of the Woulff bottle, and extending to the bottom of a cylinder which contained a little strong ammonia water, and was surrounded by a freezing mixture of snow and salt.

In our first experiment with the modified apparatus the temperature of the Woulff bottle was maintained at $132^\circ \pm 2$, and that of the ether at $12^\circ \pm 1$. 10 g. of ether were taken, and oxygen was bubbled through at such a rate that evaporation was complete in an hour and forty minutes. Assuming that the oxygen was saturated with ether vapor, the average time of exposure of the mixture to the elevated temperature was approximately ten minutes. The passage of oxygen was continued until all ether and aldehyde vapor had been swept out of the Woulff bottle. The thistle-tube was then disconnected and rinsed down into the cylinder, the contents of which consisted of an aqueous ammoniacal layer and an ether layer. These liquids were then transferred to an Erlenmeyer flask. No attempt was made to distinguish between the amount of ether which had been oxidized to aldehyde, and that which had been oxidized to acetic acid, but the total amount oxidized was determined as follows, using a modification of the method of Blank and Finkenbeiner:¹ 50 cc. of pure hydrogen peroxide and 50 cc. 0.5 *N* sodium hydroxide solution were added. The solution was warmed until oxidation of the aldehyde was complete and the excess of peroxide decomposed, then boiled until the last trace of ammonia was expelled. It was then cooled, the sides of the flask rinsed down, and the excess of sodium hydroxide titrated with 0.5 *N* sulfuric acid, using litmus as indicator. 43.3 cc. of acid were required, showing that 6.7 cc. of 0.5 *N* sodium hydroxide, equivalent to 0.47 g. of acetic acid or 0.29 g. ether, had been neutralized by the oxidation products. Hence the ether was oxidized to the extent of 2.9%.

In another experiment all conditions were maintained the same, except that a bypass for oxygen was installed, so that approximately double

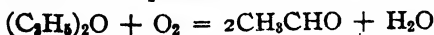
¹ *Ber.*, 31, 2979 (1898).

molecular quantities of oxygen acted on the ether vapor, and the time of the experiment was prolonged to eight hours, whereby the time of exposure of the gas mixture to the elevated temperature was considerably lengthened. We were very much surprised, on titration of our product, to find that the extent of oxidation was identical with that obtained in the former experiment, namely, 2.9%, a coincidence which we do not attempt to explain.

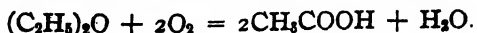
In an effort to obtain a more complete oxidation of the ether we further modified our apparatus by dispensing with the bypass for oxygen and introducing a Woulff bottle of 1400 cc. capacity in place of the smaller one. In our later experiments we maintained the temperature in the Woulff bottle at 160°. Three experiments were carried out under these conditions. In the last of these we determined on one aliquot portion of the distillate the total percentage of ether oxidized, according to the method given above, and on another aliquot the percentage oxidized to acetic acid. This last determination was made as follows: The distillate, collected as before in a cylinder containing strong aqueous ammonia, surrounded by a freezing mixture, was made up to 500 cc. and an aliquot portion of 100 cc. taken. 50 cc. of 0.5 *N* sodium hydroxide solution were added and the solution boiled until ammonia and aldehyde were expelled. A slight resinification of the aldehyde was indicated by the fact that the solution became yellow as the boiling proceeded. After all ammonia was expelled, the solution was cooled and the excess of alkali titrated with 0.5 *N* sulfuric acid, using litmus indicator. The results of the three experiments are summarized in the appended table:

| Expt. No. | Grams ether taken. | Duration of expt. Min. | Ave. time of exposure to 160° temp. | % ether oxidized | | |
|--------------|--------------------------|------------------------------|---|------------------|----------|--------|
| | | | | to ald. | to acid. | total. |
| 1..... | 10 | 160 | 35 | .. | .. | 32.5 |
| 2..... | 5 | 70 | 30 | .. | .. | 35.2 |
| 3..... | 5 | 70 | 30 | 11.6 | 23.9 | 35.5 |

As may be seen from the results of the third experiment, the major part of the aldehyde produced was further oxidized to acetic acid. Since the ether vapor and oxygen were originally present in equimolecular proportions as required for the equation



it will be seen that there was only enough oxygen present to convert one-half of the ether to acetic acid according to the equation



From the results of this experiment we see that $2 \times 23.9 + 11.6$ or 59.4% of the oxygen was used in oxidizing 35.5% of the ether. This result would indicate that the introduction of more oxygen was essential to secure complete oxidation of the ether. When, however, we attempted to carry out experiments using a larger proportion of oxygen, we found that even with initial temperatures as low as 150° the reaction was so rapid that the gas

mixture was subject to sudden rises in temperature and subsequent explosions. Consequently we were obliged to abandon the attempt to show that ether can be quantitatively oxidized under these conditions.

In an effort to check the apparent contradiction in the literature on the effect of chromic anhydride on ether, some pure chromic anhydride was prepared, and added to pure ether. A very violent reaction, with evolution of aldehyde vapors, and separation of green chromic oxide, resulted. When the ether was cooled in a freezing mixture to -10° and the chromic anhydride added, a yellow solution was momentarily produced, but reaction began almost at once with the same results as before.

Summary.

1. Ether vapor is oxidized to aldehyde and acetic acid, when heated with air or oxygen.
2. This oxidation begins at temperatures as low as 110° , and is very rapid at 160° .
3. Chromic anhydride does not dissolve without alteration in pure ether.

FORT COLLINS, COL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

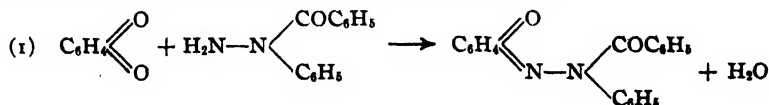
A CONTRIBUTION TO THE STUDY OF THE CONSTITUTION OF THE HYDROXYAZO COMPOUNDS. THE ACTION OF UNSYMMETRICAL BENZOYLPARATOLYLHYDRAZINE UPON BENZOQUINONE AND ITS HOMOLOGS.

BY WILLIAM MCPHERSON AND GEORGE WEATHERWORTH STRATTON.

Received March 6, 1915.

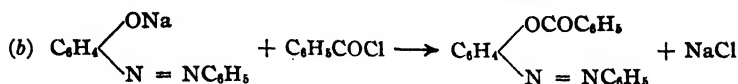
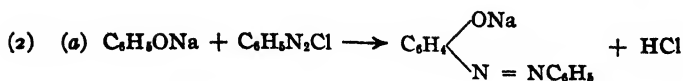
Theoretical.

It has been shown by Nef and McPherson¹ that unsymmetrical (or α) benzoylphenylhydrazine condenses with paraquinones forming the corresponding quinonehydrazones. For example, with benzoquinone the reaction is represented by the following equation:

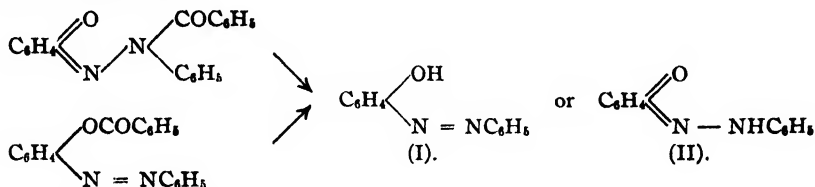


The resulting hydrazones proved to be, not identical, but isomeric with the benzoyl derivatives of the corresponding hydroxyazo-compounds. Thus the hydrazone obtained by the action of unsymmetrical benzoylphenylhydrazine on benzoquinone according to Equation 1 given above, is isomeric with the benzoyl derivative of hydroxyazobenzene prepared by the reaction expressed in the following equations:

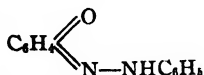
¹ *Ber.*, 28, 2418 (1895); *Am. Chem. J.*, 22, 364 (1899); 25, 485 (1901).



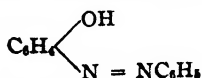
Now both the hydrazone derivative formed as represented in Equation 1 above and the isomeric hydroxyazo compound formed according to Equation 2 yield on saponification the same compound, namely, hydroxyazobenzene (benzeneazophenol). The reactions are represented by the following equations:



It is evident, therefore, that in the saponification of one of the compounds a migration of the hydrogen atom replacing the benzoyl group takes place. If the migration occurs in the hydrazone, the hydrogen atom which takes the place of the benzoyl group passing from the nitrogen to the oxygen, then the constitution of the resulting hydroxyazobenzene must be represented by Formula I. On the other hand if the migration takes place in the hydroxyazo compound then Formula II correctly represents the constitution of the hydroxyazobenzene. From the general results obtained in different investigations,¹ it seems probable that the migration actually takes place in the hydrazone and that Formula I is the correct one for hydroxyazobenzene. This indicates that the molecule represented by the formula



is unstable, rearranging as fast as formed to the more stable compound



It was thought that by varying the radicals it might be possible to obtain a stable body of the general formula, $\text{R} \begin{array}{l} \text{O} \\ \text{C} = \text{N} \end{array} \text{NHR}'$ and consistent

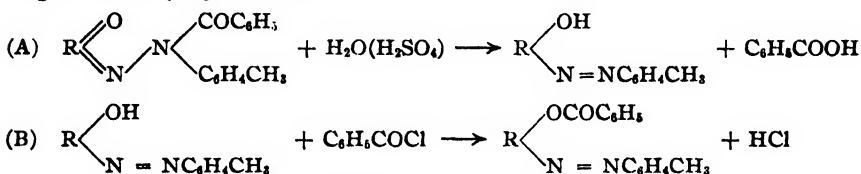
efforts have been made in this laboratory to isolate a compound of this constitution. If such a compound could be isolated, it would throw much light upon the general question of the constitution of the parent

¹ THIS JOURNAL, 33, 1525.

hydroxyazo compounds. In the present investigation, the action of the unsymmetrical benzoyl-*p*-tolylhydrazine upon some of the *p*-quinones was investigated. It was found that hydrazones are formed in accordance with the following equation:



The resulting hydrazones when saponified yield not the parent hydrazones, but hydroxyazo compounds (Equation A) and these when benzoylated (Equation B) give derivatives that are not identical but isomeric with the original benzoylhydrazones:



Experimental Part.

Preparation of *p*-Tolylhydrazine.—This is most readily obtained from *p*-toluidine by methods similar to those used in preparing phenylhydrazine from aniline. The following method gave good results: To 18 g. of *p*-toluidine was added 150 cc. of water and then 30 cc. of hydrochloric acid (sp. gr. 1.2). The resulting mixture was then stirred until all of the toluidine dissolved. The clear liquid so obtained was cooled to 5° and diazotized by the addition of the theoretical quantity of sodium nitrite (12 g.). To the resulting solution there was added, slowly at first and with constant stirring, 120 g. of stannous chloride dissolved in 100 cc. of concentrated hydrochloric acid. The tolylhydrazine hydrochloride separated out as a thick, white solid. It was removed by filtration and the filtrate salted out to obtain the hydrochloride which remained in solution. The yield of the hydrochloride was from 65 to 75% of the theoretical quantity. In order to obtain the free tolylhydrazine, the hydrochloride was neutralized with a concentrated solution of sodium hydroxide. The tolylhydrazine separated out on the surface of the liquid as a yellow oil which solidified to an almost white solid when the solution cooled. The solid was removed and the remaining solution extracted with ether in order to dissolve out any remaining hydrazine. The crude compound was purified by recrystallizing from ether.

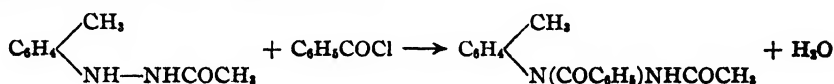
Preparation of β -Acetyl-*p*-tolylhydrazine, $\text{CH}_3\text{C}_6\text{H}_4\text{—NH—NHCOCH}_3$.—This compound was first prepared by Gattermann, Johnson and Holze¹ by boiling a solution of the tolylhydrazine in glacial acetic acid. The

¹ Ber., 25, 1080 (1892).

following method was found to give an excellent yield of the pure compound:

The theoretical quantity of acetic anhydride was slowly added to an ethereal solution of 25 g. of the tolylhydrazine. The rapid evaporation of the ether during the reaction keeps the temperature down and gives a pure product. Before all the anhydride was added the acetylhydrazine began to separate, and at the end of the experiment a large percentage of it had settled to the bottom of the vessel. This was filtered from the ether and washed once or twice with ether—a procedure which obviated the troublesome recrystallization from hot water. The pure compound melting at 130° was thus readily obtained.

α -Benzoyl- β -acetyl-*p*-tolylhydrazine, $\text{CH}_3\text{C}_6\text{H}_4\text{N}(\text{COC}_6\text{H}_5)\text{NHCOCH}_3$.—Upon benzoylating β -acetyl-*p*-tolylhydrazine in benzene solution by means of benzoyl chloride the benzoyl group enters in the α -position as shown in the following equation:



In carrying out the reaction the acetyl compound was dissolved in benzene (25 g. in 250 cc. of benzene) in a flask which was then connected with a reflux condenser. The theoretical quantity of benzoyl chloride was added through the condenser and the solution boiled until hydrogen chloride ceased to be evolved. The addition of benzoyl chloride causes the formation of a precipitate which dissolves, however, when the mixture is heated.

If the benzene solution is allowed to cool slowly the α -benzoyl- β -acetylhydrazine separates out as a hard cake which adheres firmly to the bottom of the flask. It was found better to pour the hot solution into a beaker, evaporate a portion of the benzene and cool rapidly, constantly agitating the liquid. In this way it was obtained in the form of finely divided crystals. The yield was almost quantitative.

α -Benzoyl- β -acetyl-*p*-tolylhydrazine is very slightly soluble in ligroin, rather more soluble in ether and alcohol and chloroform, and very soluble in benzene. It may be purified by crystallizing from benzene or benzene-ligroin. From these solvents it is obtained in compact nodules of small crystals, which melt sharply at 135° .

Calc. for $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2$: N, 10.45; C, 71.64; H, 5.97; found: N, 10.38; C, 71.76; H, 5.96.

α -Benzoyl-*p*-tolylhydrazine, $\text{CH}_3\text{C}_6\text{H}_4\text{—N}(\text{COC}_6\text{H}_5)\text{NH}_2$.—This compound is prepared by the saponification of α -benzoyl- β -acetyl-*p*-tolylhydrazine.

The process was carried out as follows: 25 g. of α -benzoyl- β -acetyl-

p-tolylhydrazine was placed in a flask and 150 cc. of water added. The flask was connected with a reflux condenser and the mixture heated to boiling. Alcohol was then poured in, a little at a time, until the solid was just dissolved. Sulfuric acid (25 g.) was then added and the solution boiled until the odor of ethyl benzoate could be detected. As the solution cooled the sulfate of the α -benzoyl-*p*-tolylhydrazine separated. It was always found to be mixed with some unchanged α -benzoyl- β -acetyl-*p*-tolylhydrazine. Different concentrations of sulfuric acid were tried with the idea of eliminating this difficulty, but the most satisfactory results were obtained with the dilution given.

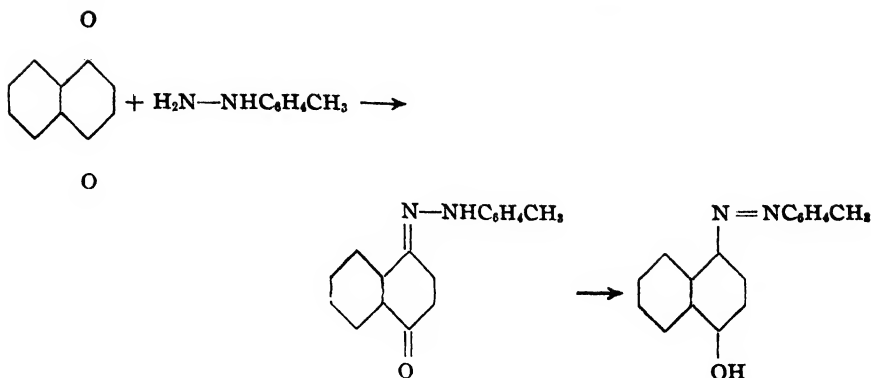
The sulfate obtained by the above process was purified by washing it first with chloroform and then with ether. It is a white solid, but slightly soluble in the common organic solvents excepting alcohol. To obtain the free hydrazine the sulfate was dissolved in dilute alcohol, neutralized with sodium carbonate and the resulting solution extracted with ether. Upon evaporation of the ether an oil was obtained which would not solidify. By extracting this oil several times with ligroin, combining the ligroin extracts and evaporating them slowly, an oil was finally obtained which, on standing for several days, changed almost entirely into fine, white crystals which were grouped together in nodules. They were purified by washing rapidly with ether. The pure α -benzoyl-*p*-tolylhydrazine thus obtained is very soluble in the common organic solvents. It melts at 68–70°.

Calc. for $C_{14}H_{14}N_2O$: N, 12.39; C, 74.34; H, 6.19; found: N, 12.32; C, 73.90; H, 6.25.

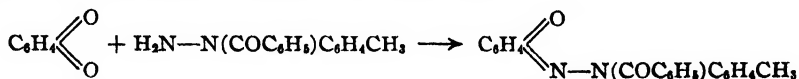
α -Benzoyl-*p*-tolylhydrazinehydrochloride.—The hydrochloride of α -benzoyl-*p*-tolylhydrazine was prepared from the free compound by dissolving the latter in benzene and passing dry hydrogen chloride into the solution. It separated out as a pinkish white solid which was purified by washing with benzene and ether.

The Action of Tolyldiazine upon *p*-Quinones.—It has long been known¹ that phenylhydrazine acts as a reducing agent upon quinones of the benzene series, converting them into the corresponding hydroquinones. With α -naphthoquinone, on the other hand, condensation takes place and a hydroxyazo compound is produced. It was found that *p*-tolylhydrazine acts in a similar way. Thus by its action in benzene solution, benzo-, tolu- and thymo-quinones are converted into the corresponding hydroquinones, while α -naphthoquinone gives tolueneazo- α -naphthol. In the first three cases nitrogen is evolved and the hydroquinones precipitate on standing. The reaction with α -naphthoquinone is represented by the following equation:

¹ Ber., 16, 1563 (1883).



The Action of α -Benzoyl-*p*-tolylhydrazine Hydrochloride (or Sulfate) on Benzoquinone; Benzoquinone- α -benzoyl-*p*-tolylhydrazone.—The sulfate or hydrochloride of α -benzoyl-*p*-tolylhydrazine condenses with benzoquinone, yielding the corresponding hydrazone:

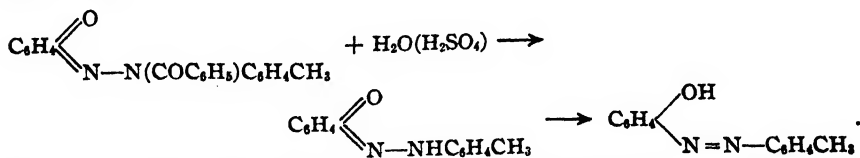


The reaction must be carried out in dilute alcoholic solution, since in concentrated solutions decomposition results.

One gram of benzoquinone was dissolved in 200–250 cc. of 95% alcohol. Water was added to this solution until the total volume was about 600 cc. To this solution was then added 4 g. of α -benzoyl-*p*-tolylhydrazine sulfate dissolved in 600 cc. of dilute alcohol of the same strength as the solvent for the quinone. The mixture was stirred and allowed to stand for 24 hours. The hydrazone separated as a yellowish solid which slowly settled to the bottom of the flask. It was filtered by suction, dried on the hot plate at 100° and recrystallized several times from benzene-ligroin and finally from ligroin. It was thus obtained in the form of finely divided, yellow crystals which melted at 141°. The yield of the crude product was 3 g. The compound is very soluble in ether, alcohol, benzene and chloroform and slightly soluble in ligroin.

Calc. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$: N, 8.86; C, 75.95; H, 5.06; found: N, 8.95; C, 75.63; H, 5.07.

Action of Saponifying Agents upon Benzoquinone- α -benzoyl-*p*-tolylhydrazone,

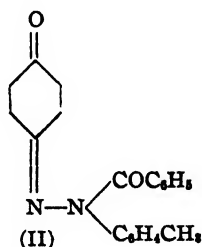
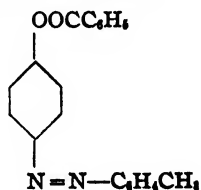


When saponified with hot alcoholic potash or concentrated sulfuric acid

the hydrazone is converted into *p*-tolueneazophenol and benzoic acid as shown in the above equation. The best results were obtained by dissolving the hydrazone in concentrated sulfuric acid and pouring the resulting solution into a large volume of water. The impure phenol separated at once. It was purified by dissolving it in a 20% sodium hydroxide solution, filtering and neutralizing the filtrate with hydrochloric acid. Further purification was accomplished by repeated recrystallization from ligroin and benzene-ligroin. The finely divided orange-yellow crystals thus obtained melted sharply at 152° . This compound was found to be identical with tolueneazophenol prepared by the action of *p*-diazotoluenechloride upon phenol. Each of the two compounds as well as a mixture of the two melted sharply at 152° . All efforts to obtain the free benzoquinone-*p*-tolylhydrazone failed, indicating its probable unstable character.

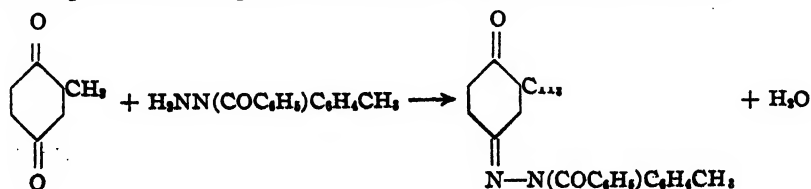
The Benzoate of *p*-Tolueneazophenol.—This compound was prepared from tolueneazophenol by the Baumann-Schotten reaction. The crude product was purified with ligroin. It forms reddish yellow needles melting at 159° .

This benzoate, according to its method of preparation, must be represented by Formula I below. It is not identical but isomeric with benzoquinone- α -benzoyl-*p*-tolylhydrazone, the constitution of which is represented by Formula II below:



The colors and crystalline forms of the two compounds as well as their melting points are different. Moreover, the melting point of a mixture of the two, while indefinite, was considerably below that of either of the pure compounds.

The Action of α -Benzoyl-*p*-tolylhydrazine on Toluquinone; Toluquinone- α -benzoyl-*p*-tolylhydrazone.—The action of the tolylhydrazine on toluquinone takes place according to the following equation:

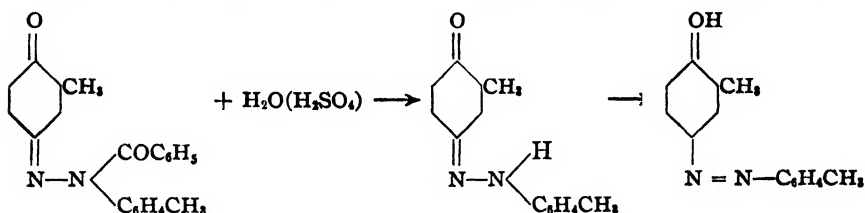


This condensation was effected under the same conditions that were used in the preparation of the corresponding benzoquinonehydrazone.

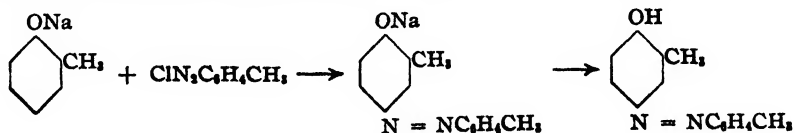
One gram of toluquinone was dissolved in 250 cc. of 95% alcohol and water added until the total volume was about 700 cc. To this solution was then added 3 g. of α -benzoyl-*p*-tolylhydrazine sulfate dissolved in 700 cc. of dilute alcohol (3 parts of 95% alcohol to 4 parts of water). The hydrazone began to separate at once and at the end of 24 hours the reaction was complete. Two grams of the crude product were obtained. Purification was effected by repeated recrystallization from ligroin and benzene-ligroin. The fine, yellow crystals obtained melted at 178°. They are somewhat lighter in color than the crystals of the corresponding benzoquinone hydrazone. The compound is very slightly soluble in dilute alcohol. It is not very soluble in ligroin but dissolves readily in other organic solvents.

Calc. for $C_{21}H_{18}N_2O_2$: N, 8.49; C, 76.37; H, 5.45; found: N, 8.53; C, 76.16; H, 5.52.

Saponification of Toluquinone- α -benzoyl-*p*-tolylhydrazone.—The saponification takes place in accordance with the following equation:

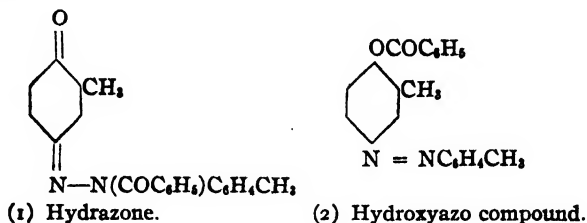


It was effected by dissolving the hydrazone in concentrated sulfuric acid and pouring the resulting solution into a large volume of water. The crude product thus obtained was treated with a 20% caustic potash solution which dissolved the hydroxyazo compound. This was reprecipitated by means of hydrochloric acid, and was purified by repeated crystallization from ligroin. In this way it was finally obtained in the form of orange-yellow crystal clusters melting at 135°. This compound was found to be identical with tolueneazo-*o*-cresol, prepared by treating a diazotized solution of *p*-toluidine with an alkaline solution of *o*-cresol:

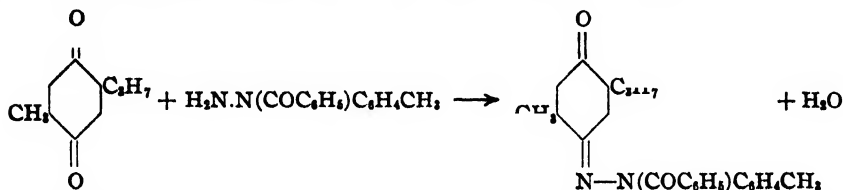


The benzoate of tolueneazo-*o*-cresol was prepared by the Baumann-Schotten method. By crystallizing from ligroin it was obtained in the form of orange-yellow crystal clusters melting at 165°. It is not identical but isomeric with the compound obtained by the action of α -benzoyl-

p-tolylhydrazine on toluquinone. The formulas of the two compounds are as follows:



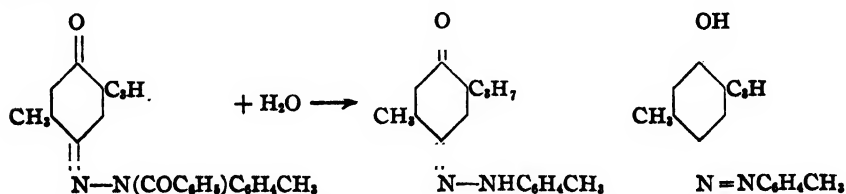
The Action of α -Benzoyl-*p*-tolylhydrazine on Thymoquinone: Thymoquinone- α -benzoyl-*p*-tolylhydrazine.—Thymoquinone condenses with benzoyl-*p*-tolylhydrazine as shown in the following equation:



The condensation was carried out in the following way: One gram of thymoquinone was dissolved in 300 cc. of 95% alcohol and the solution diluted to 700 cc. To this was added 3 g. of α -benzoyl-*p*-tolylhydrazine sulfate dissolved in dilute alcohol (3 parts of 95% alcohol to 4 parts of water). After standing 48 hours the crude hydrazone (1.5 g.) was removed by filtration and purified by repeated crystallizations from ligroin. It was obtained in the form of light yellowish green crystals melting at 125°.

Calc. for $C_{24}H_{22}N_2O_2$: N, 7.53; C, 77.42; H, 6.45; found: N, 7.78; C, 77.25; H, 6.59.

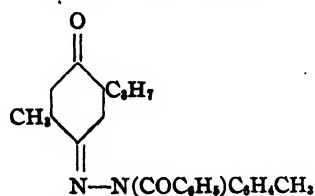
Saponification of Thymoquinone- α -Benzoyl-*p*-tolylhydrazine.—The saponification was effected both by sulfuric acid and by potassium hydroxide. In each case the reaction took place according to the following equation:



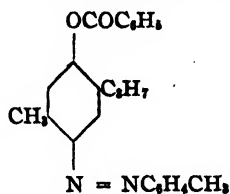
The crude product was dissolved in a dilute solution of potassium hydroxide and reprecipitated by the addition of hydrochloric acid. Finally it was crystallized a number of times from ligroin. It was then obtained in the form of yellow crystals which melted at 117°.

This compound proved to be identical with *p*-tolueneazothymol prepared in the following way: A solution of diazotoluene chloride was added to the theoretical amount of an alkaline solution of thymol. The resulting solid proved to be a mixture of the *o*- and *p*-tolueneazothymol. This mixture was treated with a solution of sodium hydroxide which dissolved the para compound only. This was then precipitated, dried and purified by crystallization from ligroin. The resulting yellow crystalline solid melted at 117° . A mixture of the solid and the product obtained by the saponification of thymoquinonebenzoyl-*p*-tolylhydrazone likewise melted sharply at 117° , thus proving the identity of the two compounds.

Upon benzoylating the tolueneazothymol according to the Baumann-Schotten method, a compound was obtained which crystallized from ligroin in short, red, needle-shaped crystals melting at 127° . A mixture of this compound and thymoquinone- α -benzoyl-*p*-tolylhydrazone melted considerably lower than either constituent. These two compounds are therefore not identical but isomeric as shown in the following formulas:



(1) Hydrazone.



(2) Hydrazo compound.

Summary.

(a).—The preparation of α -benzoyl-*p*-tolylhydrazine is given and the properties of the compound described.

(b).—The action of α -benzoyl-*p*-tolylhydrazine upon benzoquinone, toluquinone and thymoquinone is described. The resulting compounds are shown to be not identical but isomeric with the benzoyl derivatives of the corresponding compounds prepared by the action of diazotoluene chloride upon phenol, *o*-cresol and thymol, respectively.

(c).—The corresponding isomeric compounds when saponified give the same compound, namely, a hydroxyazo compound.

(d).—While it is possible to obtain the α -benzoyl derivatives of the quinone hydrazones, no evidence was obtained of the existence of the parent quinone hydrazones in stable form.

(e).—The bearing of the reactions upon the constitution of the hydroxy-azo compounds is discussed.

CICUTOXIN: THE POISONOUS PRINCIPLE IN WATER HEMLOCK (CICUTA).

By C. A. JACOBSON.

Received December 31, 1914.

Introductory.

Water hemlock is a very widely distributed poisonous plant, whose botanical character varies with its geographical location. Several different species are described as occurring, not only in the same country, but in restricted areas of the same country. Two or perhaps three distinct varieties may be recognized in this country: the eastern *Cicuta maculata* and *Cicuta bulbifera* and the western *Cicuta occidentalis*. The *maculata* appears to be identical with the tall variety of the French Ciguë Vireuse and the German Wasserschiefeling (*Cicuta virosa*). These varieties are, however, to be clearly distinguished from the spotted hemlock (*Conium maculatum*) of Socrates fame, which is a different genus.

A very complete bibliography of water hemlock literature was published by Marsh and Clawson,¹ but among the dozens of publications on the subject there is but one, namely, Pohl's,² purporting to give a chemical discussion of the poisonous principle of the plant.

The effect of the poison on frogs has been investigated by Wikszemski,³ and the effect on dogs and cats by Boehm.⁴ A great deal of experimentation on the plant has been carried out in several of our agricultural experiment stations, but with conflicting and indefinite results. The reason for this may be found in the fact that the chemical character of the poison itself has not been understood. Extractions of the plant have been made and fed to stock, and in some cases found to be poisonous, while in others not. One man states that swine are immune from the poison, another describes the death of two sows after eating the roots. In one case an experimenter fed as high as 41 pounds of the water hemlock roots to a sheep weighing 91 pounds without pronounced effects, but when he fed 2.5 pounds of the roots to another weighing 93 pounds, the sheep died. Nothing was said about the character of the roots nor when they were dug.

These are instances of the mass of conflicting data found on the subject, and the problem of undertaking to get more reliable and definite results seemed well worth while. Hendrick⁵ estimates that over 100 cattle were lost in Oregon in one year from this source, and Chestnut and Wilcox⁶ record 150 deaths among sheep and cattle in Montana in one year. Several cases of cattle poisoning and two suicides among Indians,

¹ U. S. Dept. Agric., Bull. 69.

² *Archiv. Exp. Pathol.*, 34, 262 (1894)..

³ Dissertation, Dorpat (1875).

⁴ *Archiv. Exp. Pathol.*, 5, 279 (1876).

⁵ Oregon Agr. Exp. Station, Bull. 46 (1897).

⁶ U. S. Dept. of Agric., Bull. 26.

caused by eating the roots of this plant, have come to the author's attention during the progress of this work.

The main efforts in the present investigation have been directed along purely chemical lines, although the work had to be supplemented by toxicological experiments in order to trace the poisonous constituent in the various chemical transformations. For these experiments, rabbits, cats and guinea pigs were used.

Botanical.

Water hemlock belongs to the Umbelliferae, or Parsley family. It is a bulbiferous annual plant, two to five feet tall, growing along the edges of streams, ditches and lakes, and in marshy ground. Nine or ten species

of *cicuta* have been recorded as occurring in this country. About thirty-five foreign varieties are found in the literature, a number of which are already known to be duplications.

The following experimental work was carried out with the *Cicuta vagans*, Greene, which in the opinion of the author is identical with *Cicuta occidentalis*, Greene, and whose essential parts are shown in the accompanying cut. The small greenish white to white flowers are dispersed in clusters of clusters. The leaves are compound, lanceolate and medium serrate. The stem is smooth and hollow with nodes four to eight inches



Water hemlock (*cicuta vagans*).

apart. The seed is smooth, compound and markedly ribbed, and when ripe separates easily into two carpellary parts. The rootstalk from which the stem or stems grow, varies in size from that of a hazel nut to that of a man's fist. Its shape is not uniform. It has one to four or five tapering roots and these are covered with fine, white root hairs. The rootstalk is transversely chambered and next to the layer of brown cells is a fibrovascular region containing ducts from which the poisonous liquid exudes.

Chemical.

When the water hemlock rhizome, described in the foregoing section, is cut in two, drops of a yellowish balsam-like liquid ooze out upon the cut surface. A penetrating aromatic odor is observed, which is characteristic of this substance. In about a minute the light yellowish color of the droplets changes to light red, then to ruby red and reddish brown. The color change is not wholly produced by light, nor is it an oxidation process.

This yellowish viscid liquid is the poisonous principle of the plant. It is also found in the stem, particularly in the lower portions, but in relatively small amount. A Frenchman by the name of M. Brandes, recorded by Trumel,¹ named this poison cicutoxine. At least thirty-eight years later, Prof. Boehm,² of Dorpat, Russia, apparently not aware of the Frenchman's name for the substance, renamed it with the same name. The name cicutoxin has since been woven into the literature so extensively that it would hardly seem advisable to rename it, although this could now be done upon a rational chemical basis.

Methods of Preparation.—Boehm² describes three methods for the preparation of cicutoxin, but expresses doubt as to the purity of the substance obtained by all of them. In the first method he extracts the *dried* and finely ground tubers with ether, the ethereal residue is then treated with 70% alcohol and finally extracted with petrolic ether. The petrolic ether insoluble portion he calls cicutoxin. His second method consists in the extraction of the *dried* and ground roots with boiling water and subsequent treatment of the residue with 95% alcohol and petrolic ether, while his third method employs 70% alcohol containing 10% strong ammonium hydroxide as the solvent, subsequently precipitating the poison with lead acetate.

The method employed by Pohl² differs from all three of Boehm's methods in that warm 95% alcohol is used for extracting the sliced and *air-dried* tubers. The dissolved cicutoxin is precipitated from the alcohol with lead acetate, the lead removed from the filtrate with sodium sulfate and the final residue taken up in dilute alcohol and shaken out 20–30 times with petrolic ether.

¹ *Thèse-Faculté de Médecine de Paris*, No. 239, p. 6 (1838).

² *Loc. cit.*

From the following chemical discussion it will be seen that this substance polymerizes and decomposes easily at temperatures above 50°, and especially when in contact with alcohol or hot water. Experiments have also shown that when the cicuta tubers are extracted with 95% alcohol a sugar or glucoside is extracted simultaneously with the toxic substance, which has a sweet taste, and when hydrolyzed gives a strong reduction of Fehling's solution. In fact, a yellow osazone was prepared from the water solution of one of these hydrolyses, which formed in 5-6 minutes' heating and melted with decomposition at 203-204°. It was unquestionably glucosazone.

In view of the above facts the following method of preparation was adopted for obtaining the purest possible product: The fresh water hemlock tubers were ground to a fine pulp in a meat chopper and extracted with ether at room temperature, pouring the ethereal solution from flask to flask, so as to obtain it as concentrated as possible. No attempt was made to get a complete extraction, except for one quantitative determination. The ethereal solution was dried by shaking with anhydrous copper sulfate, filtered and allowed to evaporate in the air or in a stream of dry air. The residue, after all the ether had apparently passed off, continued to lose weight for several weeks. When the loss in weight amounted to 0.05% or less for a period of 24 hours the substance was considered sufficiently dry for analytical purposes. It was discovered that the substance could be precipitated as an amorphous solid from petroleic ether (b. p. 25-45°) having a temperature of 6-10°; consequently some of the ethereal residue obtained above was dissolved in a small quantity of absolute alcohol and poured, drop by drop, with constant stirring into the cold petroleic ether. The precipitate was washed by decantation with more cold petroleic ether, the solvent allowed to drain off and the residue dried in a stream of dry air.

Combustions were run on two different lots of the poisonous product, with and without precipitating from petroleic ether, yielding the following results:

| | Grams cicutoxin. | CO ₂ . | H ₂ O. | % C. | % H. |
|---|------------------|-------------------|-------------------|--------|-------|
| (Without precipitating from petroleic ether.) | | | | | |
| Lot 1 (a)..... | 0.2804 | 0.7818 | 0.2180 | 76.04 | 8.70 |
| Lot 1 (b)..... | 0.2341 | 0.6535 | 0.1830 | 76.13 | 8.75 |
| Lot 2 (c)..... | 0.2219 | 0.6194 | 0.1701 | 75.38 | 8.34 |
| Lot 2 (d)..... | 0.2261 | 0.6287 | 0.1699 | 75.10 | 8.17 |
| | | | Mean, | 75.66 | 8.49 |
| (Precipitated from petroleic ether.) | | | | | |
| Lot 1 (e)..... | 0.2013 | 0.5618 | 0.1587 | 76.11 | 8.82 |
| Lot 2 (f)..... | 0.2075 | 0.5724 | 0.1500 | 75.23 | 8.07 |
| | | | Mean, | 75.67 | 8.44 |
| Calculated composition for C ₁₅ H ₂₂ O ₂ : | | | | 75.44% | 8.67% |

The above results go to show that the ether does not dissolve any other substance from the tubers to an appreciable extent, and that the precipitation from petrolic ether does not influence the composition of the product. The less handling, and the fewer transformations to which the substance is subjected, the purer it will be. When cicutoxin is allowed to stand in contact with alcohol for some time, especially warm alcohol, or is heated with water, it decomposes and yields a petrolic ether soluble constituent having, in alcohol, a greenish fluorescence and non-toxic properties. This substance, Boehm calls umbelliferon. It is in all probability a decomposition product of cicutoxin.

Yield.—The yield of cicutoxin obtained by the ether extraction was found to be between 0.3% and 0.4% of the weight of the green tubers.

Molecular Weight.—Molecular weight determinations were made on the purified cicutoxin, resulting as follows:

Cryoscopically, with glacial acetic acid as solvent, 268.5, 265.4, 288.2; ebullioscopically, with alcohol as solvent, 926, 418, 798; with chloroform as solvent, 601.2. The molecular weight of cicutoxin calculated from analytical results is 302.21.

Empirical Formula.— $C_{19}H_{26}O_3$.

The low values obtained for the molecular weight by the freezing-point method are in all probability due to impurities, while the high and erratic results by the boiling point are due to polymerization. In the first experiment three molecules polymerized into one, and in the last one with chloroform, two molecules. This polymerization process is continuous after the cicutoxin has been removed from the plant, but proceeds very much slower at ordinary temperatures. Complete polymerization with the accompanying decomposition destroys the toxicity of the substance. The polymerization of cicutoxin diminishes its volume without perceptibly affecting its weight.

Properties of Cicutoxin.—It is a yellowish liquid resin, viscous like ordinary cane sirup, polymerizing spontaneously into a semisolid body of a ruby-red to reddish brown color. It has an odor like that described for the rhizome, a very bitter taste which persists for several minutes. The polymerization is apparently accompanied by a disengagement of a volatile or gaseous substance, for when cicutoxin is kept in a glass-stoppered bottle the polymerization is very slow compared to what it is when exposed to the air. When the substance is kept in an evacuated desiccator over concentrated sulfuric acid, the process is the most rapid and after some hours visible decomposition sets in, shown by the liberation of gas. The substance darkens and carbonizes, the acid in the desiccator assuming a ruby-red color. The visible decomposition may be retarded or entirely inhibited by lowering the temperature, increasing the pressure, or both. It cannot be dried over sulfuric acid.

Cicutoxin is very sensitive to an increase in temperature above that

normal to its formation in the plant, and differences have been observed in the products obtained in April and October from those obtained in July and August. The former is the yellower product and the more toxic, gram for gram, but the midsummer tubers contain the larger quantity of material. When cicutoxin is heated quite rapidly in a melting-point tube, it begins to decompose at 100° , the decomposition becoming pronounced at 115° and strong at $125-130^{\circ}$. At 150° the substance chars in a few minutes. When a larger quantity of the substance is heated in a test tube connected with a delivery tube, gases come off between 120° and 148° , and at the latter temperature there seems to be a pause in the decomposition process.

Cicutoxin is readily soluble in ethyl and methyl alcohol, ether, acetone, chloroform, phenol and glacial acetic acid, but is very slightly soluble in carbon tetrachloride, benzene and petroleic ether. It is insoluble in water, glycerol and aniline.

Cicutoxin has never been obtained in crystalline form, but is precipitated as an amorphous solid when a concentrated alcoholic solution is poured, drop by drop, into a large volume of cold, low-boiling petroleic ether. When the temperature rises to about 20° , the precipitated cicutoxin melts into the original sirupy mass. It is not volatile with steam nor can it be distilled in any manner without decomposition, and consequent loss of toxicity. When pure it is neutral to litmus, phenolphthalein, congo red and sodium alizarinesulfonate, but if dissolved in alcohol and the solution allowed to stand at room temperature for a few hours, sufficient decomposition will take place to render the solution slightly acid. Cicutoxin is not an aldehyde, acid, ester, carbohydrate, anhydride, ketone or hydrocarbon, but by acetylation with acetic anhydride it shows weak alcoholic properties. When ignited it burns with a smoky flame leaving a carbonaceous residue. It unites with free bromine very energetically, with the liberation of gas, the reaction being strongly exothermic. When in solution it also takes up some bromine and iodine. It ignites spontaneously when a few drops of concentrated nitric acid are poured upon it. In contact with concentrated sulfuric acid and phosphorus trichloride it chars immediately.

Cicutoxin does not haemolyze bovine, sheep or rabbit blood. It has a specific gravity of 0.9659 at 22° , and an index of refraction of 1.5885 at 25° . Its solutions exhibit no absorption bands in the visible spectrum but a general absorption is noticed in the violet. The ultraviolet was not examined.

Tests for Cicutoxin.—No satisfactory chemical test for the detection of this poison has heretofore been submitted. Takayama,¹ however, gives the following color test: a concentrated solution of cicutoxin in

¹ *Mittel. Med. Ges. Tokyo*, 17, Heft. 6 (1903).

phenol, or a mixture of phenol and ether (3 : 1), exhibits a beautiful green color when a drop of concentrated sulfuric acid is brought in contact with it on a watch glass, changing to blue and violet by reflected light and finally to brown and reddish brown.

The author finds that this test is not entirely satisfactory because the given color changes are not only produced by the pure cicutoxin but by the polymerized and decomposed product which is no longer poisonous.

The following chemical test may be given as one not open to the above objection and, as far as the author's experience goes, is entirely characteristic for the pure cicutoxin: Add a 2% aqueous barium hydroxide solution, in small quantities, to a 5% alcoholic solution of the poison, until a voluminous precipitate appears and continue the addition till the color changes to a light green, then a few drops more, after which the solution is set aside. In from one to ten minutes the precipitate will have assumed a pea-green to olive-green color, which changes to a reddish brown (O—Shade I, Mulliken Color Standard, Sheet A), if an excess of barium hydrate has been added. On the addition of a dilute mineral acid in slight excess, the color changes to a darker red (OR—Shade I, Mulliken Color Standard, Sheet A).

For detection in stomach contents, an ethereal extraction is made and the residue tested by the above method. If the quantity allows, a subcutaneous injection of 0.05 g. of substance in dilute alcohol is given to a rabbit or guinea pig and observations made of the resulting symptoms. One-tenth this amount may be used for the production of characteristic symptoms in frogs.

Decomposition Products of Cicutoxin.—The dry distillation of cicutoxin yields a gas, between 125° and 148°, burning with a blue flame, which is not absorbed by solutions of bromine, potassium hydroxide or ammoniacal cuprous chloride. 4.7 g. material yielded 11.6 cc. of the gas, measured at 20° and 650 mm. pressure. Unsuccessful attempts were made to explode this gas with three and four volumes of oxygen. The material at hand could not be sacrificed for further attempts along this line. A previous distillation of cicutoxin (36.6 g.) had been carried out at diminished pressure, collecting the distillate in the following fractions:

| Fraction. | Temp. | Pressure. | Grams distillate. | Sp. gr. | n. |
|-----------|----------|-------------|-------------------|-----------------------|--|
| 1 | 45.5–52° | 150–100 mm. | 0.27 | 0.8316 _{24°} | 1.363 _{24°} |
| 2 | 52–85° | 135–100 mm. | 1.78 | 0.8874 _{20°} | 1.370 _{24°} |
| 3 | 110–168° | 70–64 mm. | 3.13 | 0.9360 _{20°} | { 1.4845 _{12°} 1.4812 _{21.5°} 1.4766 _{30°} 1.4726 _{40°} |
| 4 | 120–150° | 160 mm. | 3.82 | 0.9608 _{20°} | |
| 5 | 150–176° | 180 mm. | 0.80 | | |

The charred residue remaining in the flask weighed 19.37 g. Great

volumes of white and yellow fumes passed off during the distillation. These had hydrocarbon odors. Analyses made of the oil obtained in fraction 3, gave the following results:

(a) 0.3829 g. oil gave 1.0455 g. CO_2 and 0.3465 g. H_2O or C 74.47 and H 10.13;

(b) 0.4090 g. oil gave 1.1133 g. CO_2 and 0.3781 g. H_2O or C 74.24 and H 10.34.

Calc. for $\text{C}_{15}\text{H}_{21}\text{O}_2$: C, 74.58%; H, 10.12%.

The steam distillation of cicutoxin yields a colorless oil. It is only partially soluble in water, the major portion being found as a globule floating on the water in the receiver. This product has a pleasant essential-oil odor, and polymerizes in the course of a few weeks into a clear transparent semisolid resin. A combustion of this oil gave the following values:

0.2545 g. oil gave 0.7592 g. CO_2 and 0.2412 g. H_2O .

Calc. for $\text{C}_{14}\text{H}_{20}\text{O}$: C, 81.44%; H, 10.75%; found: C, 81.36; H 10.61.

Not enough material was at hand for molecular weight determinations.

When cicutoxin is treated with a fairly mild oxidizing agent such as potassium permanganate or nitric acid (1 : 3), it breaks up into various well-known substances. Pohl¹ detected oxalic acid as a decomposition product of cicutoxin, by using potassium permanganate. The correctness of his observation was confirmed by the work in this laboratory, where oxalic acid has been obtained with both permanganate and dilute nitric acid oxidations. Carbon dioxide is another product of this treatment.

In order to determine the amount of oxalic acid and carbon dioxide resulting from the oxidation, the following experiment was carried out: 0.7681 g. cicutoxin was heated in a flask on a water bath together with 50 cc. of water solution of nitric acid (1 : 2) for 24 hours, water being added from time to time, to maintain the approximate concentration of the acid. The vapors from the flask were aspirated through water, concentrated sulfuric acid and potassium hydroxide, respectively. At the end of the experiment the tubes containing the alkali gained 0.5639 g. in weight, which represented carbon dioxide. This amount, reduced to carbon, was 20.23% of the weight of the oxidized cicutoxin. There remained in the flask an unoxidized residue weighing 7.7 mg. This residue can be broken up by prolonging the oxidation. The oxalic acid was obtained from the nitric acid solution by neutralizing the latter with KOH, acidifying with acetic acid, treating with calcium chloride and titrating the oxalic acid liberated from its calcium salt, with standard potassium permanganate, giving 0.19297 g. $(\text{COOH})_2$. Assuming that the carbon atoms and one oxygen atom of the oxalic acid came from cicutoxin, it would mean that 11.27% of the cicutoxin went to oxalic acid. The ratio of $2\text{C} + \text{O}$ to $\text{C}_{15}\text{H}_{21}\text{O}_2$ is 13.23%.

Three additional products resulting from the oxidation were identified,

¹ *Loc. cit.*

namely, hydrocyanic acid, isobutyric acid and acetyl-2-cyclopentanone. The first of these was found in the wash water through which the carbon dioxide was aspirated. This acid, precipitated with silver nitrate, gave a white salt, not sensitive to light, and upon burning showed the cyanide composition. The nitrogen had been supplied by the nitric acid. When the nitric acid solution resulting from the cicutoxin oxidation was shaken with ether, the ethereal solution treated with metallic zinc to remove the dissolved nitric acid, and the filtrate from the zinc treatment allowed to evaporate at room temperature, a liquid remained, having acid properties and a decided isobutyric acid odor. This liquid was distilled, the distillate shaken out with ether and, after drying, the substance was recovered from the ether and burned, with results indicating the composition $C_4H_8O_2$.

In a subsequent oxidation of cicutoxin with nitric acid, the major portion of oxalic acid was removed by crystallization and the larger portion of nitric acid by evaporation over caustic soda. The resulting paste was extracted with ether, the ethereal solution treated with zinc as above and the resulting liquid distilled under a pressure of about 15 mm., giving a constant and sharp boiling point of 73.5° . It had a rather pleasant ethereal odor and yielded combustion values indicating the composition $C_7H_{10}O_2$. Blaise and Koehler¹ synthesized a substance with this composition, whose boiling point was 75° at 8 mm. and showed it to be acetyl-2-cyclopentanone.

Attempts at hydrolyzing the cicutoxin with dilute sulfuric and hydrochloric acids were unsuccessful, but as a result there was obtained a very inert polymerization product, which was labelled "K." The same product was evidently formed by both processes. Cicutoxin in contact with 50 times its weight of 20-25% sulfuric acid was at first heated on the water bath for a couple of hours and then subjected to steam distillation for three hours. The substance swelled, darkened and became porous like a sponge. After removal from the flask it hardened and became brittle. It was powdered and washed free of acid with boiling water, dried to constant weight and burned.

(a) 0.2021 g. "K" by H_2SO_4 gave 0.5497 g. CO_2 and 0.1414 g. H_2O .

(b) 0.1809 g. "K" by H_2SO_4 gave 0.4932 g. CO_2 and 0.1295 g. H_2O .

Mean composition from (a) and (b) C 74.27%, H 7.91%.

The same procedure was carried out with cicutoxin and 20% hydrochloric acid, yielding apparently the same "K."

0.2363 g. "K" by HCl gave 0.6474 g. CO_2 and 0.1734 g. H_2O .

Composition of "K" by HCl , C 74.75%, H 8.21%.

Calculated for $C_{17}H_{22}O_2$: C 74.40%, H 8.09%.

A similar treatment of cicutoxin with nitric acid yields a different substance, which indicates the introduction of oxygen into the polym-

¹ *Bull. Soc. Chim. de France*, 4, 7, 710 (1910).

erized product. Combustions of two different lots rendered the following values:

| | Grams "K" HNO_3 . | Grams CO_2 . | Grams H_2O . | % C. | % H. |
|--|-------------------------------|--------------------------|---------------------------------|-------|------|
| Lot 1 (a)..... | 0.1998 | 0.4028 | 0.0971 | 54.98 | 5.44 |
| Lot 1 (b)..... | 0.2036 | 0.4106 | 0.0964 | 55.00 | 5.30 |
| Lot 2 (a)..... | 0.2728 | 0.5585 | 0.1291 | 55.85 | 5.29 |
| | | | Average, | 55.28 | 5.34 |
| Calc. for $\text{C}_{15}\text{H}_{17}\text{O}_8$ | | | | 55.35 | 5.29 |

"K" obtained by the first two processes, as well as that obtained by heating cicutoxin with water in a sealed bomb tube to 200° , is one of the most stable and chemically inert substances known to the author. It is very sparingly soluble in hot ethyl and amyl alcohol, amyl acetate, naphthalene and phenol, but wholly insoluble in water, chloroform, pyridine, methyl alcohol, turpentine, carbon disulfide, carbon tetrachloride, potassium hydroxide solution, formic and acetic acids. No reagent was found to dissolve it to any appreciable extent except concentrated nitric and sulfuric acids, which destroy its identity.

The decomposition of cicutoxin with hydriodic acid (sp. gr. 1.7) was attempted in the hope of determining the number of methoxyl groups present in the compound. Various alkyl determinations were made, both with the free cicutoxin and when dissolved in glacial acetic acid, rendering values between 1.50% and 1.75% CH_3 . Judging from the molecular weight determinations and subsequent work, these values do not indicate the presence of a CH_3O - group in the molecule.

Combinations of Cicutoxin.—Besides being very unstable, cicutoxin is relatively inert and only a few combinations of definite character have been successfully made. After working with the substance for three years, Boehm¹ says he is unable to arrive at an understanding of its chemical nature. This was doubtless due to the fact that he did not recognize the great instability of the substance at temperatures above 50° , and also when dissolved in alcohol.

Cicutoxin is best precipitated from its alcoholic solution as a compound of lead or barium. The former is the more stable and definite. The barium salt seems to be a combination of the partly decomposed cicutoxin molecule, and is itself unstable. For precipitating the lead compound, a clear water or alcoholic solution of basic lead acetate is prepared, of about 10% strength, and added slowly to an alcoholic solution of cicutoxin at room temperature, producing immediately a light yellow precipitate. The reagent is added until no further precipitation results. The precipitate is first washed by decantation and then on a filter paper with 50% alcohol until the filtrate is free from lead. The compound

¹ *Loc. cit.*

does not melt, but begins to decompose and char at about 230° . It ignites spontaneously when concentrated nitric acid is added to it.

| | Gram Pb salt. | Gram PbSO ₄ . | Gram CO ₂ . | Gram H ₂ O. | % Pb. | % C. | % H. |
|--|------------------|-----------------------------|---------------------------|---------------------------|-------|-------|------|
| (a)..... | 0.2062 | 0.1136 | | | 37.63 | ... | |
| (b)..... | 0.2040 | 0.1131 | | | 37.87 | ... | |
| (c)..... | 0.2103 | | 0.3289 | 0.0825 | ... | 42.65 | 4.39 |
| (d)..... | 0.2238 | | 0.3550 | 0.0927 | ... | 43.26 | 4.61 |
| Calc. for C ₁₉ H ₂₇ O ₅ Pb..... | | | | | 38.19 | 42.04 | 5.01 |

The barium salt is made by slowly adding a 5% aqueous barium hydroxide solution to a dilute solution of cicutoxin in alcohol, at room temperature, with constant stirring. A yellowish precipitate at first appears, which turns greenish to dark green after the point of saturation has been reached and the solution becomes slightly alkaline. This precipitate settles slowly and is stable towards alcohol and water so that the compound may be washed as in the case of the lead salt, but if the barium hydrate is added to excess the color of the precipitate changes to nearly that of Shade I, Yellow-Orange, in Mulliken's Color Standards. If an excess of acid is added to the barium salt, a reddish brown sirupy substance resembling the original material separates out. The above observations would indicate that the barium salt thus obtained is unstable and that great importance cannot be attached to the values obtained for its composition. With a little experience one may be able to interrupt the precipitation at the right moment, so that a compound of uniform composition can be obtained. When this barium salt is kept for some months in a desiccator, or in the open air, the green color gradually fades into a sandy brown.

The washed and dried barium salt yielded the following analytical values:

| | Gram Ba salt. | Gram CO ₂ . | Gram H ₂ O. | Gram BaSO ₄ . | % C. | % H. | % Ba. |
|--|------------------|---------------------------|---------------------------|-----------------------------|-------|------|-------|
| (a)..... | 0.2100 | 0.4305 | 0.1053 | | 55.91 | 5.61 | ... |
| (b)..... | 0.2036 | 0.4182 | 0.0998 | | 56.02 | 5.49 | ... |
| (c)..... | 0.3762 | | | 0.1488 | ... | ... | 23.29 |
| (d)..... | 0.3926 | | | 0.1566 | ... | ... | 23.47 |
| Calc. for (C ₁₄ H ₁₇ O ₃) ₂ Ba..... | | | | | 55.66 | 5.68 | 22.75 |

The barium salt behaves like the lead salt in the melting-point tube, charring above 200° .

According to preliminary tests, cicutoxin possesses alcoholic properties, therefore attempts were made to produce a pure acetyl product of the poison. Both acetic anhydride and acetyl chloride were used but it was found that the latter reagent was the more adaptable. A dilute solution of cicutoxin in glacial acetic acid was made and acetyl chloride added in excess. The solution turned from a ruby-red to a dark brown, with a faint tint of green, but yielded no precipitate. The reaction mixture

was evaporated to dryness at a low temperature. The brown residue was dissolved in a small amount of hot alcohol and precipitated from low-boiling petroleic ether. This was repeated and then the brown powder dried in a desiccator to constant weight and burned.

(a) 0.2016 and 0.2019 g. acetyl prod. gave 0.5012 and 0.5216 g. CO_2 ; 0.1266 and 0.1300 g. H_2O .

Calc. for $\text{C}_{14}\text{H}_{16}\text{O}_3(\text{OCCH}_3)_2$: C 67.89%, H 6.97%; found: C 67.80, 69.09 and H 7.03, 7.07.

The acetyl product also precipitates from the alcoholic solution upon cooling, and this might have been a better method for the purification of the substance.

The iodine value of cicutoxin was found according to Hübl, the mean of two determinations being 125.5. Assuming the molecular weight of the substance to be 302.21, three atoms of iodine entered the molecule. The number obtained by calculation, using the above iodine value, was 2.99.

The bromine and iodine derivatives of cicutoxin have been made but they are difficult to purify, and a good deal of variation in the halogen content of different lots have been found, so that too much weight should not be attached to these determinations. The iodine compound, which is the more satisfactory to work with, is made by adding a dilute solution of iodine in glacial acetic acid to a solution of cicutoxin in the same solvent. Almost immediately a brown precipitate settles out, which is washed free of iodine with carbon tetrachloride. The substance is further purified by extracting with ether, until the latter solvent remains colorless. The ether removes a small amount of a substance that contains iodine. The ether insoluble residue is then dried and subjected to analysis. The compound ignites spontaneously when heated to 100° .

| | Gram I comp. | Gram AgI. | % I. | | Gram I comp. | Gram CO_2 . | Gram H_2O . | % C. | % H. | % I. |
|--|-----------------|--------------|-------|-----|-----------------|-------------------------|--------------------------------|-------|-------|------------|
| (a) | 0.1997 | 0.1394 | 37.76 | (d) | 0.2043 | 0.3522 | 0.0813 | 47.02 | 4.46 | |
| (b) | 0.2000 | 0.1311 | 35.43 | (e) | 0.2028 | 0.3493 | 0.0910 | 46.97 | 5.02 | |
| (c) | 0.2215 | 0.1450 | 35.38 | (f) | 0.2079 | 0.3566 | 0.0851 | 46.78 | 4.58 | |
| | | | | | | | | Mean, | 46.94 | 4.69 |
| Calc. for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{I}$ | | | | | | | | | 46.66 | 4.76 35.25 |

The bromine compound was made similar to the iodine, but in this case a dark brown to black liquid separated. This was purified in a similar way to the one above, but it was difficult to wash free of bromine and almost impossible to dry. Carius' determinations on this product yielded 22.15% and 23.53% bromine. The percentage of bromine calculated for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{Br}$ is 25.54, showing that the composition is not far remote from that suggested by the iodine product.

It was found that the halogen acids form addition products with cicu-

toxin, or, more correctly, with a modified form of the cicutoxin molecule. The hydrochloride of cicutoxin was made by passing dry hydrochloric acid gas into a solution of the substance in absolute alcohol until the solution became saturated at the temperature of an ice-salt mixture. After saturation the flask was kept in the freezing mixture for 24 hours, with the hope of getting a crystalline product to separate, but without success. The dark brown solution resulting was evaporated to dryness at about 50°, the residue taken up in ether and shaken free of hydrochloric acid with water. The ethereal solution was then dried with calcium chloride and evaporated to dryness, leaving a brown amorphous powder which was subjected to analysis.

| | Gram salt. | Gram AgCl. | %Cl. | Gram. CO ₂ . | Gram. H ₂ O. | % C. | % H. | Cl. |
|---|---------------|---------------|-------|----------------------------|----------------------------|---------|--------|-------|
| Lot 1 (a).... | 0.2254 | 0.1225 | 13.44 | ... | | ... | | |
| Lot 1 (b).... | 0.2355 | 0.1292 | 13.54 | ... | | ... | | |
| Lot 2 (c).... | 0.2248 | 0.1212 | 13.31 | ... | | ... | | |
| Lot 1 (d).... | 0.1847 | | ... | 0.4705 | 0.1246 | 69.47 | (7.55) | |
| Lot 2 (e).... | 0.2269 | | ... | 0.5682 | 0.1688 | (68.30) | 8.33 | |
| Lot 3 (f).... | 0.2346 | | ... | 0.5986 | 0.1691 | 69.59 | 8.07 | |
| Lot 3 (g).... | 0.2534 | | ... | 0.6474 | 0.1917 | 69.68 | 8.55 | |
| Mean, | | | | | | 69.51 | 8.29 | |
| Calc. for C ₃₁ H ₄₂ O ₃ .2HCl..... | | | | | | 69.50 | 8.29 | 13.25 |

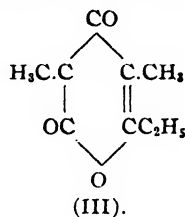
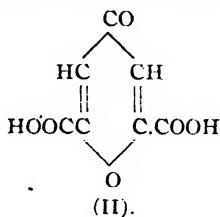
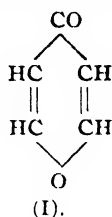
The amine hydrochloride of cicutoxin was prepared by saturating the alcoholic solution with dry ammonia gas and heating to 165° in a sealed bomb for two hours. The resulting solution was treated with an excess of hydrochloric acid, evaporated to dryness and the residue taken up in ether, washed with water and the substance precipitated from a mixture of low-boiling petrolic ether and carbon tetrachloride (three to one, by volume). The resulting brown product was washed, dried and subjected to analysis with the following results:

0.1985 g. subs. gave 0.1061 g. AgCl which is 13.22% Cl.
 0.4487 g. subs. gave by Dumas' method, 19.6 cc. N at 26° and 646.2 mm. pressure, equivalent to 4.07% N.
 (a) 0.1642 g. subs. gave 0.3952 g. CO₂ and 0.1000 g. H₂O equals C 65.64 and H 6.82.
 (b) 0.1871 g. subs. gave 0.4519 g. CO₂ and 0.1134 g. H₂O equals C 65.87 and H 6.78.
 Calc. for C₃₁H₄₂O₃.N₃Cl₄: C 65.71%, H 6.83%, N 3.90%, Cl 13.16%.

Structure of the Molecule.—Recognizing that no constitutional formula can be ascribed with certainty to a complex molecule upon purely analytical data, yet when a certain familiarity with a substance is gained, combined with a knowledge of a large number of transformations, it would seem justifiable to incorporate that knowledge into an expression best explaining the facts known. Besides the facts recorded in this paper the author has made countless observations upon cicutoxin and its chemical behavior. Four-fifths or more of the experiments undertaken with the substance

have been negative or inconclusive and therefore omitted from this discussion. Each observation, however, whether positive or negative, has contributed to its knowledge.

More and more as the facts accumulated the author was led to believe that in the molecule of cicutoxin he had a pyrone nucleus to deal with. γ -Pyrone has the constitution shown in (I), in which one or more hydrogen



atoms may be substituted by an element or group, retaining the double linkage between the two pairs of carbon atoms as in chelidonic acid (II). One side of the molecule may be saturated by another pair of elements or groups as in α -ethyl- β,β' -dimethylpyrone (III), which was synthesized by Wedekind.¹

According to the records of Brühl,² Willstätter and Pummerer,³ Hantzsch and Denstorff,⁴ Feist and Baum,⁵ Staudinger,⁶ Ruhemann⁷ and others, concerning pyrone and its derivatives, a marked similarity in properties exists between this class of substances and cicutoxin. Both classes polymerize and change color in the air and especially when heated, both oxidize and yield oxalic acid quite readily, both are unsaturated and have indefinite basicity, both have carbonyl oxygen without yielding an oxime or phenylhydrazone, both add halogen acids and salts, but not free halogens, both substitute halogens for hydrogen, their iodine substitution products being very stable, with high melting points. Both classes form colored salts with certain basic elements and both substitute oxygen for the nitrogen in ammonia. These, together with some other minor similarities, have led the author to believe that cicutoxin is a derivative of γ -pyrone.

The reason for not being able to isolate and determine this constituent may be found in the fact that unstable groups are attached to the pyrone nucleus, which break up and effect immediate polymerization when the molecule is subjected to higher temperatures or chemical treatment. This explanation becomes more plausible when one considers the character

¹ *Ann.*, **378**, 261 (1911).

² *Ber.*, **24**, 2450 (1891).

³ *Ibid.*, **37**, 3740 (1904).

⁴ *Ibid.*, **40**, 241 (1907).

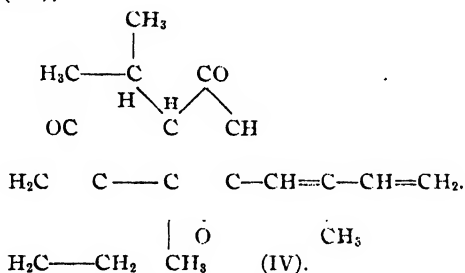
⁵ *Ibid.*, **38**, 3562 (1905).

⁶ *Ann.*, **380**, 288 (1911); **384**, 62 (1911).

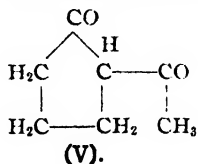
⁷ *J. Chem. Soc.*, **75**, 415 (1899).

of these groups and the extraordinary stability of the polymerization product "K."

We then have the following building material out of which to construct the graphic molecule: a pyrone nucleus, an acetyl-2-cyclopentanone group, an isobutyl group, which when oxidized away would yield either isobutyric aldehyde or isobutyric acid. In case the former resulted it would, according to Taipale,¹ be oxidized to isobutyric acid by the hydrocyanic acid shown to be present. Besides these, an unsaturated and unstable group must be introduced on purely empirical grounds, which is chosen only after careful consideration of its properties and the transformations it is likely to occasion. In view, therefore, of the facts adduced, the author feels justified to submit the following structural formula for the cicutoxin molecule (IV),



This expression corresponds to the empirical formula $\text{C}_{19}\text{H}_{26}\text{O}_8$ obtained by analysis. The lower left hand radical is cyclopentanone containing a labile hydrogen atom, making it tautomeric with cyclopentanol, in which condition the formation of the acetyl product and barium salt are rendered possible. The same condition of tautomerism is presumed for the β' -hydrogen atom of the pyrone ring, shifting to the γ -position under certain conditions. The decomposition product obtained from the nitric acid oxidation was acetyl-2-cyclopentanone, shown in (V), instead of the straight pentanone, shown as a radical in (IV).

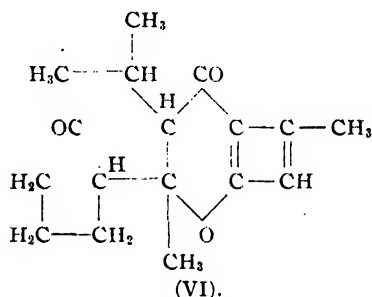


Since the pyrone molecule is far less stable than the five-membered carbon ring it is obvious that, when the molecule is split up by the nitric acid, the break should occur at the most vulnerable place. We therefore have the isobutyl group liberated and oxidized to isobutyric aldehyde or acid, the pentanone group split off, taking with it the oxygen and α' -carbon atoms of the pyrone together with the attached methyl. The

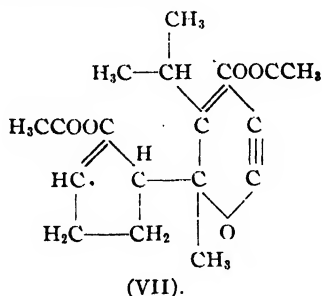
¹ J. Russ. Phys. Chem. Ges., 41, 815 (1909).

rest of the molecule is oxidized to oxalic acid and carbon dioxide, with the exception of a carbon-hydrogen group which forms hydrocyanic acid with the nitrogen from nitric acid, and one or more hydrocarbons that are undoubtedly liberated in the polymerization immediately preceding the oxidation.

The right hand isoprene group is the most unstable part of the entire molecule. Isoprene decomposes readily under certain circumstances and polymerizes under others, and these properties especially fit the conditions of the cicutoxin molecule. Suppose the isoprene radical should be split in two, liberating C_2H_4 , and the free bond of the isoprene carbon unite with the β -carbon of the pyrone ring, we should get the structure represented in (VI).



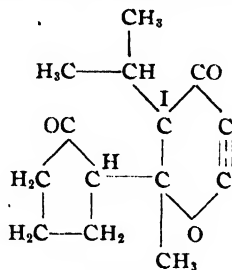
If this molecule should polymerize, which is not beyond the range of possibility, we would have a product whose composition would be that of "K," or $(C_{17}H_{22}O_3)_x$. On the other hand, if under certain conditions, particularly an acid medium, the entire isoprene group were to be removed and acetyl groups substituted for the two labile hydrogens, we should get the form represented in (VII), which has the same composition as the acetyl product isolated from cicutoxin.¹



The iodine product obtained may be represented by the same formula,

¹ NOTE.—An objection to this formula may be made on the ground that the introduction of a triple bond in the pyrone nucleus is unprecedented, but it is nevertheless within the range of possibility. It has already been noted that, although pyrone contains double bonds, it does not add halogen, and this property is apparently not changed by the introduction of a triple bond.

one iodine being substituted for the β' -hydrogen in the pyrone ring and the isoprene group eliminated as shown in (VIII).



(VIII).

The lead salt of cicutoxin may be considered as having been formed like the neutral salt combinations with pyrone itself in which oxonium compounds have resulted. In this case the PbO and OH groups from the basic lead acetate are in the same manner supposed to satisfy the quadrivalent oxygen of the pyrone nucleus making the formula for the lead salt $\text{C}_{19}\text{H}_{26}\text{O}_3 \cdot \text{PbO} \cdot \text{OH}$. Descriptions of somewhat similar organic lead oxide combinations may be found in the literature,¹ but too much credence should not be placed on either the lead or the barium salt for the reason that their purification could not be accomplished satisfactorily. The barium salt is not supposed to be an oxonium compound, like the lead salt and the hydrochloride, but a cyclopentanolate, obtained by the substitution of the cyclopentanol hydrogen in two molecules of cicutoxin. No doubt other alkali and alkaline earth salts of the same composition are formed although their isolation proved unsuccessful.

It has already been pointed out that in a mineral acid medium cicutoxin easily decomposes, with a recombination or polymerization of certain parts resulting from the decomposition. Consequently, it was not to be expected that a straight hydrochloride or amine hydrochloride of the substance could be made. However, the hydrochloride obtained bears a simple relation to certain decomposition products obtained from cicutoxin. The product "K," obtained from a mineral acid medium, is considered some multiple of $\text{C}_{17}\text{H}_{22}\text{O}_3$. If this group were to combine with the oil obtained by steam distillation ($\text{C}_{14}\text{H}_{22}\text{O}$), with the elimination of H_2O , and if this compound molecule should add two molecules of hydrochloric acid, we would get a compound corresponding to the analytical values obtained for the hydrochloride made from cicutoxin.

Not so simple a relation as this is disclosed by the composition of the amine hydrochloride, but the analytical values for this compound have been included without attempting to show what the relation is. It is

¹ *Jahresber. Chem.*, 16, 566 (1863); *Ann.*, 255, 195 (1890); *Deutsche Zucker Industrie*, 12, 1367.

not improbable that this product is the hydrochloride of a modified imino cicutoxin corresponding to pyridone which is obtained from pyrone with ammonia, or oxypicolinic acid obtained from comanic acid.

It is interesting to note that chelidonic acid, a simple derivative of pyrone, has been isolated from the roots of the poisonous veratrum or white hellebore belonging to the lily family, a plant also growing in swamps and marshy ground.

Toxicological.¹

A fairly concordant literature is found on the physiological effects of this poison. With the exception of the frog, the symptoms are very similar in all the lower animals, as well as man. Cicutoxin may be classed as a narcotic cramp poison which attacks certain brain centers.

Three well-defined stages of symptoms are recognized in *cicuta* poisoning, namely, a prodromal, a paroxysmal and a paralytic stage. The first represents the time prior to the beginning of visible symptoms, and is usually not of more than forty minutes' duration.

When the poison is administered intravenously the animal at once passes into the second or paroxysmal stage, beginning with a strong salivation and tremors. The animal is then seized by convulsions at irregular intervals, characterized by violent chewing and frothing at the mouth. The tonic and clonic spasms, into which the animal is thrown, render it unconscious and irresponsive to stimulation. There is also dilation of the pupils, a more rapid and shallow respiration, as well as an increase in body temperature. This stage usually lasts from twenty minutes to six or eight hours.

The paralytic or final stage represents the time when the animal has relapsed into total paralysis and is no further responsive to stimulation. This stage is only of a few minutes' duration.

Wikszemski² has shown that cicutoxin attacks the cramp center of the brain, located at the base of the fourth ventricle. It also affects the pneumogastric centre so that a small dose stimulates and a larger one paralyzes the action of the lungs and heart. The animal dies from asphyxiation and exhaustion.

In regard to the toxicity of the poison it has been found that a root the size of a walnut is sufficient to kill a cow. 150-200 mg. cicutoxin kills the average rabbit and 200 mg. the average cat. Boehm² found that, per kilo body weight of dogs, 110 mg. per mouth and 21 mg. intravenously, was sufficient to kill; and that 50 mg. per kilo body weight of cats, when administered per mouth, was found sufficient to kill. From other in-

¹ A detailed account of the botanical and toxicological investigations of water hemlock will be published in *Bulletin* 81 of The Nevada Agricultural Experiment Station.

² *Loc. cit.*

vestigations, however, it would appear that the lethal dose of this poison cannot be correctly given in terms of milligrams per kilo body weight.

No abnormalities whatsoever are noticed after death, with the exception of a pronounced venous hyperemia of the brain and lungs, and in certain cases, a reddening of the inside lining of the stomach.

No antidote for cicutoxin is known. The most successful treatment, in human cases of poisoning, consists in producing vomiting and moderating the effects of the convulsions by means of a narcotic, such as morphine or opium.

The author wishes to acknowledge the assistance of Mr. August Holmes, during the major portion of this work.

Conclusion.

Water hemlock is an umbelliferous, poisonous plant, growing along the banks of streams and in marshy ground. It is recognized under at least three distinct species in this country, all three containing the same poisonous principle, cicutoxin, which is located primarily in the rhizome or root-stalk of the plant.

Cicutoxin is an unstable resin-like substance of the formula $C_{19}H_{26}O_3$, and is a complex derivative of pyrone. A tentative structural formula for the cicutoxin molecule has been proposed. It decomposes and polymerizes readily, especially at temperatures above 50° . It is extracted from the tubers by means of ether and enters violently into combination with free bromine.

It forms combinations with lead, barium, hydrochloric acid, ammonia, and yields the double acetyl derivative.

A reliable chemical test for its presence has been found.

Cicutoxin is a spasmotoxin, producing symptoms that may be separated into a prodromal, a paroxysmal and a paralytic stage. Death ordinarily results in from thirty minutes to eight hours. The lethal dose of cicutoxin for the average rabbit is 175 mg., and "50 mg. per kilo body weight" for cats, when administered per mouth. Cicutoxin attacks a nerve center in the calamus scriptorius and kills by asphyxiation and exhaustion.

It is not a constitutional poison and the lethal dose cannot properly be given in terms of milligrams per kilo body weight. No antidote is known for this poison, and the most reliable treatment at present consists in producing vomiting and allaying the convulsions by means of a narcotic.

RENO, NEV.

¹ NOTE.—In order to make the knowledge of this plant as complete as possible, any information regarding its character, distribution and harmfulness will be gratefully received by the author and duly acknowledged in a subsequent paper or bulletin.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

A NEW SYNTHESIS OF IMINOACETONITRILE AND ITS CONVERSION TO HYDRAZINODIACETIC ACID.

By J. R. BAILEY AND D. F. SNYDER.

Received February 8, 1915.

Introduction.

From the work of various investigators¹ it appeared highly probable that methyleneaminoacetonitrile, $\text{CH}_2 = \text{NCH}_2\text{CN}$,² would readily add on prussic acid, and thus furnish an excellent method for the preparation of iminoacetonitrile, $\text{NH}(\text{CH}_2\text{CN})_2$.³ Our first experiment in this direction showed that the expected reaction proceeds normally at room temperature, when the above methyleneamino compound is subjected to the action of either absolute or an aqueous prussic acid. This method of preparing the nitrile of iminodiacetic acid, on account of the ease with which the starting substances can be obtained, and, because of the fact that the reaction proceeds quantitatively without the formation of other products, may supplement the method of Eschweiler, referred to above, where, in the treatment of hexamethylenetetramine with prussic acid under different conditions, aminoacetonitrile, iminoacetonitrile, and nitrilotriacetonitrile, $\text{N}(\text{CH}_2\text{CN})_3$, are formed in varying amounts. Strangely enough, M. Delépine states that methyleneaminoacetonitrile is indifferent to prussic acid.⁴ This investigator showed that ethylidene- α -propionitrile, $\text{CH}_3\text{CH} = \text{NCH}(\text{CH}_3)\text{CN}$, and numerous alkylidene amines add on prussic acid; but, after trying under modified conditions to effect the reaction that, according to our observation proceeds so smoothly between methyleneaminoacetonitrile and prussic acid, he reported as follows: "J'ai constaté que ce corps ($\text{CH}_2 = \text{NCH}_2\text{CN}$) restait absolument inaltéré sous l'influence de l'acide cyanhydrique à froid, en présence ou en l'absence de solvants." Delépine advances the supposed resistance of methyleneaminoacetonitrile towards prussic acid in support of the dimeric formula proposed by Klages for this substance.⁵ In case Klages' view of the molecular weight of methyleneaminoacetonitrile be correct, and we have no reason to doubt the correctness of his conclusion in this matter, we must ascribe to the prussic acid in the above reaction a depolymerizing action which probably precedes the additive action. A molecular weight determination showed conclusively that iminoacetonitrile is monomolecular. Granting that methyleneaminoacetonitrile is dimolecular, no insight into the constitution of the molecule is afforded by its chemical behavior be-

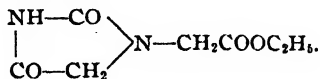
¹ *Ber.*, 25, 2020 (1892); *Ann.*, 283, 11 (1894); 290, 1 (1896); 303, 75 (1898).² *Ber.*, 27, 59 (1894).³ *Ann.*, 278, 229 (1894).⁴ *Bull. soc. chim.*, 29, 1202 (1903).⁵ *J. prakt. Chem.*, [2] 65, 192 (1902).

cause depolymerization always accompanies its chemical changes. Frequently the group $N = C$ in polymerized molecules takes up HCN with the resultant addition product monomolecular, as in the above case investigated by us. Von Miller with his co-workers¹ found that anhydroformaldehyde aniline, although trimolecular, and dimeric anhydrovaleraldehyde aniline showed the behavior toward prussic acid of simple monomolecular compounds, yielding anilidoacetonitrile and anilidovaleronitrile, respectively. Ethylideneaniline, on the other hand, proved indifferent to prussic acid. Furthermore, unpublished experiments conducted in this laboratory show that the complex insoluble reaction product of formaldehyde with hydrazine is not in any way altered by prussic acid.² Delépine observed that the polymeric condition of alkylidene amines at lower temperatures is not always of moment in their behavior toward HCN, as he found that "the polymerized molecules frequently react like the simple molecules."³

Attempts were made by us in the preparation of iminoacetonitrile to generate the prussic acid from KCN and HCl in the presence of the methyleneaminoacetonitrile, and thus simplify the process. However, as is frequently the case in the conversion of the complex $N = C$ to $NH-CCN$ by the addition of HCN, the desired result was not attained by this method.

Knoevenagel⁴ has shown that aldehyde bisulfite compounds condense with amines with the elimination of water, forming salts of substituted aminomethane sulfonic acids of the general formula $R_2NCH(R)SO_3Na$. These latter substances react readily with potassium cyanide, yielding substitution products of aminoacetonitrile of the general formula, $R_2NCH(R)CN$. It appeared probable that a like result might be attained by adding alkali bisulfite on to the $N = C$ complex in methyleneaminoacetonitrile, and then treating the reaction product with KCN. As shown in the experimental part of this article, iminoacetonitrile may be made in this way, but the conditions were not established under which a satisfactory yield could be obtained.

A very comprehensive investigation of iminoacetonitrile has been carried out by Jongkees.⁴ In the course of his work he converted the nitrile to ethyl hydantoino-1-acetate,



We have been able to improve on his rather complicated process in the preparation of this substance, in that, by treatment of iminoacetonitrile in glacial acetic acid with potassium cyanate, saponification of the ureido

¹ *Loc. cit.*

² Observation of L. A. Mikeska.

³ *Ber.*, 37, 4073 (1904).

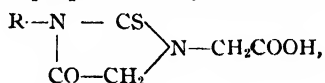
⁴ *Rec. trav. chim.*, 27, 287 (1908).

derivative thus formed, and then esterification, we pass directly from iminoacetoneitrile to the above ethyl hydantoinoacetate with a 45% yield, and without the isolation of the intermediary products. This process can no doubt be employed in converting other imino acid nitriles into the corresponding hydantoino acid esters. The use of glacial acetic acid as a solvent in effecting the urea synthesis was first tried in this laboratory in an investigation of the action of cyanic acid on hydrazo-*i*-butyric acid, $(\text{CH}_3)_2\text{CNHNHC}(\text{CH}_3)_2$, the results of which work will



be published shortly. Experiments were tried without result to convert iminoacetoneitrile to its ureido derivative in the usual way, by the action of potassium cyanate on the hydrochloride of this amine in water solution.

The H in the NH group of iminoacetoneitrile, in contrast to the imino hydrogen in the corresponding acid, is very reactive, but, especially where an elevated temperature is required to replace this hydrogen, a disturbing factor enters in the case of the nitrile, owing to the ease with which this substance splits off HCN. Although iminodiacetic acid has been known a long time,¹ no investigator has announced the preparation of corresponding thiohydantoin from this imino acid and mustard oils. As Marckwald, Neumark, and Stelzner² have shown that, in the case of the aliphatic amino acids, it is necessary to salify the carboxyl before the NH_2 group will react readily with mustard oils, it appeared probable that salts of iminodiacetic acid, in contrast to the free acid, would condense with mustard oils. We find that by using the acid sodium salt of iminodiacetic acid, it is very easy to prepare thiohydantoin of the general formula



which can be readily isolated in the form of their ethyl esters.

Our work on the derivatives of iminodiacetic acid had its origin in the problem of working out a method of passing from imino diacids to hydrazinodiacids, corresponding to hydrazinodiacetic acid, $\text{NH}_2\text{N}(\text{CH}_2\text{COOH})_2$. This hydrazine, discovered by Curtius and Hussong,³ readily yields with nitrous acid iminodiacetic acid: $\text{NH}_2\text{N}(\text{CH}_2\text{COOH})_2 + \text{HNO}_2 = \text{NH}(\text{CH}_2\text{COOH})_2 + \text{N}_2\text{O} + \text{H}_2\text{O}$.⁴ From the work of Fischer,⁵ Renouf,⁶ and Harries⁷ on the reduction of nitrosamines, it appeared highly

¹ *Ann.*, **122**, 257 (1862).

² *Ber.*, **24**, 3278 (1892).

³ *J. prakt. Chem.*, [2] **83**, 270 (1911).

⁴ *THIS JOURNAL*, **36**, 1759 (1914).

⁵ *Ann.*, **190**, 146 (1878).

⁶ *Ibid.*, **199**, 308 (1879).

⁷ *Ber.*, **28**, 1223 (1895).

probable that iminodiacetic acid could be reconverted to hydrazinodiacetic acid by reducing nitrosiminodiacetic acid. Working with methyl nitrosiminodiacetate, $\text{NON}(\text{CH}_2\text{COOCH}_3)_2$, we have obtained hydrazinodiacetic acid by reduction with sodium amalgam, and experiments are being carried out in this laboratory directed towards the extension of this process to the preparation of other hydrazino diacids. Although this method is of no preparative value in the above case, where it has been applied, it will doubtless prove of value in preparing some of the higher homologs in this series.

Experimental Part.

Preparation of Iminoacetonitrile from Methyleneaminoacetonitrile and Prussic Acid.—100 cc. of absolute prussic acid, containing 10 drops of concentrated hydrochloric acid, are poured on 100 g. of methyleneaminoacetonitrile in a thick-walled pressure flask. In about twenty-four hours complete solution is effected, and then later on the iminoacetonitrile begins to crystallize out in an interwoven mass of long prisms. At the end of forty-eight hours the excess of prussic acid is recovered by distilling it off below 50° , and finally a further small amount is removed from the nitrile by allowing it to stand *in vacuo*. The compound is then purified by recrystallization from acetic ether, and finally from benzene. Petroleic ether is an excellent solvent for purification, where small amounts of the nitrile are to be identified, as even from smears it can be regained colorless in long, hair-like needles by the use of this solvent. Prepared in the above way, iminoacetonitrile melts sharply and undecomposed at 75° , as determined by Eschweiler. In working with this substance the fact should be borne in mind that on prolonged heating in solvents, it evolves prussic acid. As a further identification of the preparation obtained by the action of prussic acid on methyleneaminoacetonitrile, it was converted according to the directions of Eschweiler into the corresponding acid, and into the characteristic hydrochloride of the methyl ester described by Jongkees. The following analysis and molecular weight determinations were made on the nitrile prepared by the new process:

Calc. for $\text{C}_4\text{H}_6\text{N}_3$: C, 50.53; H, 5.26; N, 44.21; found: C, 50.67; H, 5.36; N, 44.39.

Three molecular weight determinations by the freezing point method with acetic acid as the solvent gave 105, 107, and 106. Calc. for $\text{C}_4\text{H}_6\text{N}_3$: 95.

The following modifications of making iminoacetonitrile as described above were tried in the hope of obviating the use of free prussic acid: One gram of methyleneaminoacetonitrile and 1 g. of KCN were dissolved in the least amount of water at 60° , and then 1 mol of HCl allowed to drop into the solution. Not a trace of iminoacetonitrile could be detected, but considerable unchanged methylene compound was recovered. In a second experiment 1 g. of methyleneaminoacetonitrile was stirred into a solution of sodium bisulfite, prepared from 0.8 g. of Na_2CO_3 and 2.7 g.

of water in the usual way. The methylene compound dissolved readily with an elevation of temperature of 15° , so that there is little doubt that in this process the bisulfite adds onto the $N = C$ complex. The new substance can be precipitated along with inorganic admixtures by the addition of alcohol, but, because of its ready solubility in water and its insolubility in organic solvents, a method of purification was not found. However, when the reaction mixture of bisulfite and the methylene compound was treated with one mol of KCN in water solution at 60° , the solution concentrated to a pasty consistency *in vacuo* on a water bath, and the residue extracted with petroleic ether, a considerable amount of iminoacetonitrile was obtained.

Salts of Iminoacetonitrile.—The only salt of iminoacetonitrile described in the literature is the hydrochloride, which, according to Eschweiler, precipitates on leading hydrochloric acid gas into an ether solution of the nitrile.¹ We found that a convenient way to prepare this salt is to dissolve the nitrile in 20% $CH_3OH-HCl$ by slightly warming. In a few minutes after solution, the nitrile separates as the hydrochloride in characteristic long prisms.

A more stable salt than the hydrochloride is the nitrate, which may be prepared as follows: 1 g. of the nitrile is dissolved in 4 cc. of concentrated nitric acid, and the precipitation of the salt effected by the addition of 4 cc. of absolute alcohol. For purification the nitrate is dissolved in boiling alcohol, and then precipitated by the addition of ether. It crystallizes from alcohol in very long slender needles, which melt at $134-135^{\circ}$, apparently undecomposed, but in a few seconds the liquid blackens with gas evolution. The nitrate, like the hydrochloride, hydrolizes in water solution, from which, on shaking out with ether, the free iminoacetonitrile may be regained.

Calc. for $C_2H_3O_2N_4$: C, 30.38; H, 3.80; N, 35.44; found: C, 30.70; H, 3.98; N, 35.65.

Nitrosiminoacetonitrile, $NON(CH_2CN)_2$.—If to 1 g. of iminoacetonitrile in 10.5 cc. of $N H_2SO_4$ a concentrated solution of 0.75 g. of $NaNO_2$ be added, there separates immediately a light yellow oil, which on cooling and stirring solidifies. The nitrosamine thus obtained gives the Liebermann reaction. It is more difficultly soluble than the parent substance in all solvents. For analysis it was purified by precipitation from an acetic ether solution by the addition of petroleic ether, as well as by recrystallization from benzene. It crystallizes in the form of slender prisms of a faint yellow color, melting undecomposed at 38° . Suessarew gives $51-52^{\circ}$ as the melting point of nitroso- α -iminoisobutyronitrile,² while Passavant describes nitroso- α -iminopropionitrile as an oil.³ The melting point of

¹ *Ann.*, **278**, 231 (1894).

² *J. prakt. Chem.*, [2] **89**, 364 (1914).

³ *Ann.*, **200**, 131 (1880).

iminopropionitrile lies between that of the corresponding iminonitriles of Eschweiler and Snessarew, so that in all probability the nitroso derivative of iminopropionitrile can be obtained as a solid like the above homologs. Our attempts to reduce nitrosiminoacetonitrile with sodium amalgam to hydrazinodiacetonitrile, and isolate the latter in the form of the corresponding difficultly soluble hydrazinodiacetic acid have thus far failed, because the nitroso compound is decomposed in the alkaline solution. However, further attempts will be made to establish conditions under which a reduction can be effected. Despite the fact that this nitrosamine appears perfectly stable, none of the analyses, which were made on three different preparations, agreed closely with the calculated percentages, and it may be that the melting point given above will be found too low, when carried out on a perfectly pure sample.

Calc. for $C_4H_5ON_4$: C, 38.71; H, 3.23; N, 45.16; found: C, 39.31; 39.19, 39.19; H, 3.32, 3.39, 3.31; N, 44.88, 44.45, 44.50.

Benzoyliminoacetonitrile, $C_6H_5CON(CH_2CN)_2$. — Jongkees obtained acetyliminoacetonitrile as a viscous oil, boiling at 227° under 16 mm. pressure, but was unable to make the substance crystallize. We find that the benzoyl derivative in contrast to the acetyl compound is a beautifully crystallizing substance, which can be readily prepared from iminoacetonitrile in benzene solution by heating it with one mol of benzoyl chloride. The benzoyl derivative thus prepared is readily soluble in alcohol, chloroform, acetic ether, and water, and difficultly soluble in ether and benzene. Recrystallized from alcohol, it is obtained in diamond shaped prisms, made up apparently of laminated plates, melting undecomposed at $131-132^\circ$.

Calc. for $C_{11}H_9ON_3$: C, 66.33; H, 4.52; N, 21.11; found: C, 66.08; H, 4.68; N, 21.25.

Ethyl Hydantoino-1-acetate, $CO-N-CH_2COOC_2H_5$. — 2 g. of finely powdered

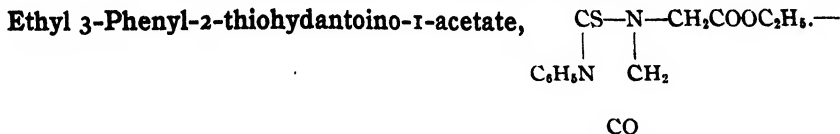
$$\begin{array}{c} CO-N-CH_2COOC_2H_5 \\ | \quad | \\ NH \quad CH_2 \end{array}$$

CO

dered potassium cyanate are stirred into a solution of 2 g. of iminoacetonitrile in 20 cc. of glacial acetic acid, whereupon reaction proceeds with a temperature elevation of about 16° . After several hours' standing, the mixture is evaporated to dryness *in vacuo*, the residue saponified by boiling with 20 cc. of concentrated hydrochloric acid, the solution again evaporated to dryness, and finally the hydantoino acetic acid esterified by boiling for two hours with 50 cc. of 5% $C_2H_5OH-HCl$. After driving off the alcohol, the hydrochloride of the ester is dissolved in a little water, the solution made just alkaline with ammonia, and then the ester extracted with chloroform. The substance, purified by recrystallization from alcohol and benzene, corresponded in its properties with the prepara

tion obtained by Jongkees with carboxymethyliminoacetonitrile, $\text{CH}_3\text{OCON}(\text{CH}_3\text{CN})_2$ as the starting substance.¹ Our yield of hydantoin ester by the above process was about 44% of the theoretical. The same substance was obtained by the action of sodium ethoxide on methyl ureidodiacetate in ethyl alcohol solution.² As a further confirmation of the constitution of the ethyl hydantoinoacetate prepared by us, a nitrogen determination was made.

Calc. for $\text{C}_7\text{H}_{10}\text{O}_4\text{N}_2$: N, 15.05; found: N, 15.35.



For the preparation of this hydantoin, 2 g. of iminoacetonitrile, dissolved in 2 mols of *N* NaOH, are allowed to stand 48 hours, and then the solution is boiled until there is no further escape of ammonia. One-half of the alkali is now neutralized with HCl, the solution evaporated to a small volume, 2.8 g. of phenyl mustard oil in 20 cc. of alcohol added, and the mixture boiled under a return condenser for 6 hours. The solution is next evaporated to dryness, and the residue containing the hydantoin esterified by boiling it with 50 cc. of 5% $\text{C}_2\text{H}_5\text{OH}-\text{HCl}$ for 2 hours, and then proceeding just as in the preparation of the above ethyl hydantoinoacetate. The yield obtained on the thiohydantoin was about 72% of the theoretical. It crystallizes from alcohol in long, slender prisms with dome-shaped end faces, which melt undecomposed at 134° . The compound is difficultly soluble in water and readily soluble in the common organic solvents, petroleic ether excepted.

Calc. for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{N}_2\text{S}$: C, 56.12; H, 5.04; N, 10.07; S, 11.51; found: C, 56.27; H, 5.25; N, 10.28; S, 11.49.

Ethyl-3-Methyl-2-thiohydantoino-1-acetate.—This hydantoin, prepared by the use of methyl mustard oil similarly to the phenyl compound, can be recrystallized from petroleic ether in the form of slender needles, which melt undecomposed at 62° . The methyl hydantoin is readily soluble in all the common solvents.

Calc. for $\text{C}_8\text{H}_{12}\text{O}_3\text{N}_2\text{S}$: N, 12.92; found: N, 13.06.

Preparation of Hydrazinodiacetic Acid from Methyl Nitrosoimino-diacetate.—0.5 g. of $\text{HCl}-\text{NH}(\text{CH}_2\text{COOCH}_3)_2$, prepared according to the method of Jongkees¹ were dissolved in 10 cc. of water, and to this solution 1.75 g. of NaNO_2 in 2 cc. of water were added. 3.5 g. of methyl nitrosoiminodiacetate separated as a yellow oil, heavier than water. No analysis was made on this preparation, as it is described in an article by Curtius,

¹ *Loc. cit.*

² See the following article.

Darapsky and Mueller.¹ The 3.5 g. of crude nitroso compound, obtained in the above experiment, were dissolved in 29 cc. of 50% alcohol, and reduced at 10° by introducing 50 g. of 5° sodium amalgam in small portions, with constant shaking. After the amalgam had become exhausted, 10 cc. of water were added and the solution, poured off from the mercury, was boiled a few minutes. On making the solution just acid with HCl, 0.6 g. of almost pure hydrazinodiacetic acid crystallized out. Reduction of the aqueous solution, from which the 3.5 g. of nitroso compound separated, with 25 g. of amalgam yielded an additional 0.3 g. of the hydrazino acid. The substance proved identical in every respect with a sample of hydrazinodiacetic acid, made from hydrazine hydrate and monochloroacetic acid.² The following analysis was made on the sample obtained in the above reduction and purified by recrystallization from water:

Calc. for $C_4H_8O_4N_2$: N, 18.92; found: N, 18.88.

AUSTIN, TEXAS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

THE NITROSO DERIVATIVES OF SEMICARBAZINODIACETIC ACID ESTERS.

By J. R. BAILEY AND D. F. SNYDER.

Received February 8, 1915.

Introduction.

In studying the relation between the derivatives of hydrazinodiacetic acid and those of iminodiacetic acid, we had occasion to repeat the work of Bailey and Read³ on the action of nitrous acid on methyl semicarbazinodiacetate. They showed that in this reaction methyl iminodiacetate is formed, but did not succeed in isolating the intermediary nitroso compound, $NH_2CON(NO)N(CH_2COOCH_3)_2$. We find that this primary reaction product can be isolated and analyzed, but after a few hours standing undergoes spontaneous decomposition as follows:



The constitution of this new substance as methyl ureidodiacetate was established by its synthesis from the hydrochloride of methyl iminodiacetate⁴ and potassium cyanate, as well as by its conversion to esters of hydantoino-1-acetic acid.⁵ In the sodium alcoholate condensation of methyl ureidodiacetate to a hydantoin,⁶ it was found that the methyl

¹ *Ber.*, 41, 356 (1908).

² *J. prakt. Chem.*, [2] 83, 271 (1911); *THIS JOURNAL*, 36, 1747 (1914).

³ *THIS JOURNAL*, 36, 1747 (1914).

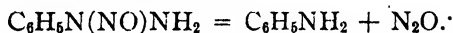
⁴ *Rec. trav. chim.*, 27, 287 (1908).

⁵ See foregoing article of Bailey and Snyder.

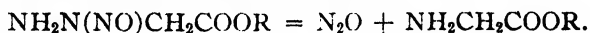
⁶ *Cf. Am. Chem. J.*, 28, 386 (1902).

ureido ester in ethyl alcohol with sodium ethoxide gave the *ethyl* ester of hydantoino-1-acetic acid, while sodium methoxide acted on the substance in methyl alcohol with the formation of the *methyl* ester of hydantoino-1-acetic acid. Bailey and Read observed a similar interchange of alkyls in the triazine condensation of methyl and ethyl semicarbazinodiacetate.¹

Fischer, in describing the spontaneous decomposition of nitrosodiethyl-semicarbazide, $\text{NH}_2\text{CON}(\text{NO})\text{N}(\text{C}_2\text{H}_5)_2$, states "these crystals can be filtered and washed, but not dried; after remaining a short time in a desiccator, they lose their yellow color and change with gas evolution to a colorless, strongly alkaline liquid."² It is probable that *unsym.*-diethylurea, $\text{NH}_2\text{CON}(\text{C}_2\text{H}_5)_2$ was formed in this decomposition, and that the alkaline reaction was due to small amounts of diethylamine and ammonia. Furthermore, in describing the nitroso derivative of methylphenylsemicarbazide, which he was able to analyze, Fischer states: "It melts at 77° with slight gas evolution and changes to a dark yellow oil, which was not further investigated."³ Here the decomposition would be expected to yield *unsym.*-methylphenylurea. Thiele⁴ has shown that α -nitroso-phenylhydrazine on heating in nitrobenzene solution decomposes quantitatively into nitrous oxide and aniline,



Darapsky and Prabhaker⁵ observed a similar decomposition on heating the esters of α -nitrosohydrazinoacetic acid *in vacuo*, in that nitrous oxide and esters of aminoacetic acid were formed,



Further investigation may show that, in conformity with the above uniform decomposition of nitroso hydrazino derivatives, it is possible in all such cases to eliminate nitrous oxide and unite the two rests joined to either side of the =NNO complex.

The decomposition in water solution of the nitroso derivatives of all secondary semicarbazino derivatives thus far investigated proceeds with the hydrolysis of the ureido group and the evolution of nitrous oxide, as first observed by Fischer, *e. g.*,



In conformity with this reaction, Bailey and Read found that methyl nitrososemicarbazinodiacetate in water solution decomposes normally as follows:

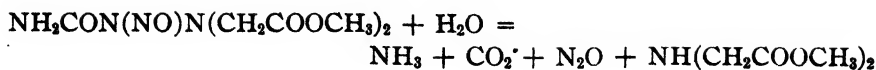
¹ THIS JOURNAL, 36, 1754 (1914).

² *Ann.*, 199, 313 (1879).

³ *Ibid.*, 190, 165 (1878).

⁴ *Ber.*, 41, 2809 (1908).

⁵ *Ibid.*, 45, 1658 (1912).



Experimental Part.

Methyl Nitrososemicarbazinodiacetate,

$\text{NH}_2\text{CON}(\text{NO})\text{N}(\text{CH}_2\text{COOCH}_3)_2$.—Methyl semicarbazinodiacetate is dissolved in five times its weight of water, a concentrated solution of one mol. of NaNO_2 added, and to this mixture kept cool in ice water, one mol of 3 *N* H_2SO_4 gradually added with constant shaking. The nitroso compound requires about one hour for complete separation. It is readily soluble in alcohol, chloroform, and benzene, and is best purified by recrystallization from acetic ether. In order that it may dry quickly, it is well to wash the nitroso compound with ether after filtering from the acetic ether. From acetic ether, it crystallizes in very characteristic tetragonal prisms of a deep yellow color, which melt with decomposition at $67\frac{1}{2}^\circ$. Even after careful purification, the substance must be kept in a cool place to preserve it sufficiently long for an analysis.

Calc. for $\text{C}_7\text{H}_{12}\text{O}_6\text{N}_4$: C, 33.87; H, 4.84; N, 22.58; found: C, 34.01; H, 4.99; N, 22.67.

Ethyl Nitrososemicarbazinodiacetate.—This nitroso derivative is prepared similarly to the above methyl ester, with the exception that here it is possible to work with the semicarbazide in an equal weight of water and, therefore, to obtain a better yield of the nitroso compound, about 1.4 g. from 2 g. of ethyl semicarbazinodiacetate. This compound possesses a remarkable difference in its solubilities in ether within a short range of temperature. It was found that a saturated solution of the nitroso compound in ether at 27° , on cooling to 5° , solidified so compactly that the test tube in which it was contained could be inverted without any loss of substance. The nitroso derivative was obtained in this way in a very pure state as a matted mass of hair-like needles, melting with decomposition at 60° .

Calc. for $\text{C}_9\text{H}_{16}\text{O}_6\text{N}_4$: N, 20.29; found: N, 20.25.

Methyl Ureidodiacetate from Methyl Nitrososemicarbazinodiacetate.

—Of the above nitroso compounds the methyl ester is the better suited for the isolation of the ureidodiacetate. For the preparation of methyl ureidodiacetate, methyl nitrososemicarbazinodiacetate is allowed to stand over sulfuric acid in a desiccator, slightly open to the air. After a short time, depending no doubt in a large measure on the temperature, gas evolution commences with a rise of temperature and the decomposition proceeds quickly to completion. The residue is then washed with a very little chloroform, which removes a small amount of smear and effects crystallization, and the ureido compound is then readily purified by crystallization from alcohol. Methyl ureidodiacetate is difficultly

soluble in ether and benzene, and readily soluble in the other common solvents with the exception of petroleic ether. From alcohol it crystallizes in prisms with dome-shaped end faces and melts at 145° with the elimination of alcohol and formation of methyl hydantoino-1-acetate.

Methyl Ureidodiacetate from the Hydrochloride of Methyl Iminodiacetate and Potassium Cyanate.—Potassium cyanate and the hydrochloride of methyl iminodiacetate react readily in concentrated aqueous solution. The ureido compound separates out in large part, and a further amount can be obtained by evaporating the solution to dryness and extracting with alcohol. This preparation proved identical with the decomposition product of methyl nitrososemicarbazinodiacetate.

Calc. for $C_7H_{12}O_5N_2$: C, 41.18; H, 5.88; N, 13.73; found: C, 41.20; H, 5.95; N, 13.91.

Conversion of Methyl Ureidodiacetate to the Methyl and Ethyl Esters to Hydantoino-1-acetic Acid.—One gram of methyl ureidodiacetate in 10 cc. of ethyl alcohol is treated with a solution of sodium ethoxide prepared from 0.12 g. of sodium. After the alcoholic solution has stood for one hour, it is neutralized with hydrochloric acid, the alcohol distilled off *in vacuo*, and the residue extracted with chloroform. The substance thus prepared and purified by recrystallization from benzene, proved identical with ethyl hydantoino-1-acetate, described in the foregoing article. Methyl ureidodiacetate in methyl alcohol gave with sodium methoxide the corresponding hydantoino methyl ester. However, a better method of preparing the latter substance is to heat methyl ureidodiacetate at 170° as long as alcohol is given off. The methyl hydantoino-1-acetate, purified by recrystallization from alcohol was obtained in prisms, melting at 114° . Jongkees, who first prepared this hydantoin, gave $107-108^{\circ}$ as its melting point. As a further confirmation of the constitution of the substance, as obtained by us, a complete analysis was made.

Calc. for $C_6H_8O_4N_2$: C, 41.86; H, 4.65; N, 16.28; found: C, 42.05; H, 4.72; N, 16.44.

Ethyl Ureidodiacetate.—The decomposition of ethyl nitrososemicarbazinodiacetate yielded a viscous residue, which on dissolving in benzene and precipitating with petroleic ether, separated as a smear. However, after this smear had stood several weeks, large irregular shaped crystals separated out. An attempt was made to identify this product, which was obtained in poor yield, as ethyl ureidodiacetate by synthesizing it in a way similar to that employed above for methyl ureidodiacetate. For this purpose the hydrochloride of ethyl iminodiacetate, made according to the method of Jongkees, was treated in aqueous solution with potassium cyanate and a substance extracted with chloroform from the solution, corresponding in solubilities and crystalline form to the decompo-

sition product of ethyl nitrososemicarbazinodiacetate. However, the latter substance melted at 80° and the ureido compound from the hydrochloride of ethyl iminodiacetate at 76° . On mixing the two preparations, dissolving the mixture in chloroform, and precipitating with petroleic ether, the substance obtained melted at 80° . It would, therefore, seem that ethyl ureidodiacetate can exist in two forms, but our available supply of ethyl semicarbazinodiacetate did not admit of the preparation of sufficient of the higher melting stable form to enable a further confirmation of this view by an analysis. Both preparations were found readily soluble in the common solvents with the exception of ether and petroleic ether and both separated from chloroform solution on addition of petroleic ether in characteristic flat prisms with dome-shaped end faces. The following analysis was made on the preparation from the hydrochloride of ethyl iminodiacetate and potassium cyanate:

Calc. for $C_9H_{16}O_5N_3$: N, 12.07; found: N, 12.28.

AUSTIN, TEXAS.

[FROM THE INSTITUTE DOYEN, PARIS.]

A STUDY OF THE NINHYDRIN REACTION IN RELATION TO THE AGE AND HABITS OF INDIVIDUALS.

BY JOKICHI TAKAMINE, JR.

Received January 21, 1915.

According to Abderhalden, the blood contains a specific "Shutzferment,"¹ which lies latent in the blood but ever ready to be brought into activity when the proper conditions prevail. Such conditions are the numerous various diseases common to the human and animal kingdom. He has shown this by experiment—The ferment only being brought into mobility when a certain specific substratum was brought into contact with it and often no other.²

But it is not easy to conceive of the blood containing a vast number of ferments each labeled for a certain disease or group of diseases. Be that as it may, Abderhalden has shown that the blood contains a ferment only brought into activity by some special and extraneous agency. Following his method of procedure, I have determined that there is a ferment, the amount of which predominates in people of old age as compared to the amount of said ferment in young people. The amount of this ferment seems to be in direct ratio to the age of the person.

To incite the release of this ferment I have used human fibroma tissue with best results, but ordinary connective tissue will also cause similar action. I have also noted with interest that the habits of the persons whose serum was tested had a direct result upon the amount of ferment

¹ *Handbuch der Biochemischen Arbeitsmethoden*, 1912, Vol. 6, p. 223.

² *Z. physiol. Chem.*, 81, 90.

present or released. For example, drinkers gave tests more positive than persons of the same age with normal habits, again persons with syphilis—a disease most depletory—also gave relatively strong tests.

That this ferment is different from the "Shutzferment" is explained by its absolute absence in humans and animals (normal) of young age. Also that the "Shutzferment" cannot so greatly augment in old age—because it is at that time that we are less easily able to withstand the ravages of disease.

Therefore, for the above reasons, I have concluded that there is a ferment other than the "Shutzferment of Abderhalden" which is shown by the ninhydrin reaction to be in direct relation to the age and habits of individuals.

It is well to give here an example of one series of experiments showing the increasing amount of "ferment" with increase of age, and also the relatively great amount in the serum of a great drinker of intoxicants and a young man with syphilis.

Series No. 7.

| | | | | |
|---|--------------|-------------|------------|---------------|
| 1 | M. B. | 17 yrs. old | No disease | No habits |
| 2 | Mme. J. | 27 yrs. old | No disease | Very healthy |
| 3 | M. P. | 21 yrs. old | Syphilis | Syphilis |
| 4 | Mme. V. | 36 yrs. old | No disease | No habits |
| 5 | Mme. I. | 49 yrs. old | No disease | Heavy drinker |
| 6 | M. V. | 50 yrs. old | No disease | No habits |
| 7 | Mme. N. | 73 yrs. old | No disease | No habits |

The method¹ I will briefly state.

The serum, taken as sterile as possible, is allowed to stand in an ice chest until there is separation of the serum and clot. The former is twice centrifuged and 1.5 cc. is placed in a "Dialyser-Hülse" of Abderhalden, with about one gram of fibroma tissue. The fibroma tissue is prepared, by first washing free from blood, then boiling in distilled water. The water is changed and to the fresh water a little acetic acid is added and the solution boiled for one minute. If this water with the acetic acid gives no biuret reaction, the fibroma tissue is ready for use—placed in a sterile flask and covered with a layer of toluene. The dialyser, now containing the serum, fibroma and a little toluene is placed in a small reagent glass containing 20 cc. of distilled water and is allowed to stand at 39° for 10 hours. 10 cc. of the water solution is then boiled in a test tube with 0.2 cc. of a 1% solution of triketohydrindenhydrate for one minute.

A positive reaction means the binding of an amino group of the ferment to the ninhydrin in the X position to the carboxyl group. This combination forms a purple coloration.

¹ *Beitrage zur Klinik der Infektionskrankheiten und zur Immunitätsforschung*, 1913, p. 243.

RESULTS FROM SERIES NO. 7.

| No. | | Contents of dialyser. | With ninhydrin. |
|--------|------------------------|-----------------------------------|-----------------|
| 1..... | (a)..... | 1.5 cc. serum 1 g. fibroma tissue | — |
| | (b)..... | 1.5 cc. serum alone (control) | — |
| 2..... | | 1.5 cc. serum alone (control) | — |
| 3..... | | 1.5 cc. serum alone (control) | +++ |
| 4..... | | 1.5 cc. serum alone (control) | + |
| 5..... | | 1.5 cc. serum alone (control) | +++ |
| 6..... | | 1.5 cc. serum alone (control) | ++ |
| 7..... | | 1.5 cc. serum alone (control) | ++++ |
| | ++++ very strong test. | +++ strong test: | ++ medium test: |
| | + weak test: | — no test. | |

From the above series we find the following results:

1. That below the age of 27 years in healthy persons the ferment is not present or at least not sensible to tests.

2. That No. 3, aged 21, and syphilitic, gave a stronger test than a man and woman (normal) aged 36 and 49, respectively.

3. That No. 7 gave by far the strongest test, being alone due to the old age ferment.

4. That No. 6 of middle age gave a test of medium strength—he was a man of no habits.

5. That No. 5 of middle age gave an extraordinarily strong test—but she was a heavy drinker.

Experiments similar to the above were made on the serum of 68 persons with similar results.

Next it was interesting to note that the amount of the ferment was also in direct ratio to the age in animals.

An interesting series of experiments was tried with the blood of rats of different ages. Their blood serum was tested with rat sarcoma, tissue provided from the laboratories of Professors Ehrlich and Bashford, which was most active in giving a positive test with rat serum, with other albuminous matter such as human adenofibroma tissue and ordinary human connective tissue the results were generally negative. Very young rats of 85–100 grams gave no tests, rats of medium age, 115–130 grams, gave tests of medium strength, sometimes negative, and rats of old age gave strong tests.

1. The blood serum of 74 rats of 85–100 g.—always negative test.

2. The blood serum of 28 rats of 115 to 130 g.—weak positive.

3. The blood serum of 42 rats of 150–250—always strong positive test.

Note.—Controls of the serum alone and of the sarcoma tissue alone were always negative.

Experiments were tried on the blood of the horse and rabbit with similar results. The blood of a one month rabbit was tested in comparison to a rabbit of one year, the connective tissue of rabbits being used, with the

result that the blood of the young rabbit gave no test while that of the older gave an exceedingly strong test. Like results were obtained with the blood of a young and an old horse, the connective tissue of the horse being used.

Much speculation and many theories may be evolved to explain the significance of this ferment. But until it is isolated and its specific properties examined—work on which I am now engaged—nothing exact can be stated. Its connection with the fibrin ferment is doubtful, in that the coagulative power is greater in young and strong people than in people of older age—and since the coagulation is directly due to the fibrin ferment we see that this is in direct opposition to the action of the ferment.

Its presence may be due to the leucocytes and I have found that causing leucocytes in rabbits the blood gives stronger tests, but I have not yet determined the relative positivity of tests on young and old rabbits with leucocytes.

From my numerous experiments with the blood of human beings and animals I have found that there is a ferment in the blood shown by the ninhydrin reaction which is in direct quantitative relation to the age and habits of individuals.

Finally the test for this ferment is particularly interesting as a diagnosis of old age.

550 WEST 173RD ST., NEW YORK CITY.

NEW BOOKS.

A Laboratory Manual for the Detection of Poisons and Powerful Drugs. By WILHELM AUTENRIETH. Authorized translation of the completely revised fourth German edition, by William H. Warren. Philadelphia: P. Blakiston's Son & Co. 320 pp., 25 illus. Price, \$2.00.

This well-known book comes to us in its fourth edition, entirely revised. The subject is divided into seven chapters, and there had been considerable rearrangement of the material. After discussing poisons volatile with steam, organic poisons, and metallic poisons, the author includes in Chap. IV, a number of substances, which seldom appear in toxicological investigations, but which have much theoretical importance. Such substances as cantharidin, ergot, santonin, sulfonal, saponin substances, and the toxalbumins have become of sufficient importance to warrant a discussion here.

Special methods of analysis both qualitative and quantitative, such as methods for the determination of arsenic and antimony, salicylic acid, and special alkaloids are discussed in the next chapter. The translator has here added the Gutzeit method for the detection of arsenic and antimony, as worked out in detail by Professor Sanger. Chapter VI will prove of special interest to Pharmacists and manufacturing chemists, as it contains a very satisfactory résumé of the methods in use for the quanti-

tative estimation of alkaloids and other powerful substances in raw materials. Since the toxicologist is often called upon to examine blood stains, the remaining chapter is devoted to this subject.

One valuable feature of the work for advanced students is the brief description of the synthesis of such organic drugs as acetanilide, anti-pyrine, phenacetine, pyramidone, salicylic acid, sulfonal, and veronal; substances that are continually coming into more common use.

It is suggested that in a future edition a more complete and detailed index would add to the value of the work. A student of medicine and toxicology will find this book an exceedingly valuable addition to his library.

E. H. S. BAILEY.

Kurzes Lehrbuch der Organischen Chemie. By A. BERNTHSEN, with A. DARAPSKY. 12 editions. Braunschweig: Friedrich Vieweg and Sohn, 1914. Pp. xix + 672. 8°. Price, unbound, M. 12; bound, M. 13.

The present volume forms the twelfth edition of this well-known and widely used text-book; the first edition appeared twenty-seven years ago. As a text-book, it is rapidly approaching the time when it will rival the *Course de Chemie* of Nicholas Lemery which appeared in 1675, passed through many editions, and served as a standard text-book for over fifty years.

To one familiar with the early editions of this book, the pages present an air of familiarity. Unlike many other German text-books, this one has not changed essentially in form, except to include recent discoveries and to make corrections in constants and data, and has not grown beyond the bounds which a self-respecting text-book should preserve. The fifth edition (1895) contained 572 pages; so that, in passing through seven editions, the book has accumulated only one hundred pages, and is still far from deserving the more pretentious title of *Handbuch*.

In the preface to the first edition, the author made the claim that the treatment "at least in the first half of the book" was "a purely inductive" one. Upon perusal of the pages of the text, however, it is hard to find any consistent application of this principle; in fact, it is probably true that no text-book of Organic Chemistry has ever been written in which the subject matter has been presented from an inductive point of view. The treatment throughout the book is especially characterized by a thorough-going formality, which, no doubt, has been the reason why this book has appealed particularly to students who have already completed an introductory course in Organic Chemistry, and to those who are compelled to review the subject with the purpose of familiarizing themselves as rapidly as possible with the systematic arrangement and typical reactions of the various classes and series of organic compounds. As might be expected, a few atavisms still cling to the pages of this most recent edition. Thus two (2) is chosen as the molecular weight of hydrogen, and as the

basis of molecular weights; the old nomenclature and formulas are used for substituted ammonium compounds, *e. g.*, "aniline hydrochloride, $C_6H_5NH_2$, HCl ," instead of phenylammonium chloride. Other illustrations of a similar character might be chosen.

Here and there throughout the book, the reader finds that the results of new and striking discoveries, recently made, have not been overlooked in revising the text. A few, chosen at random, will serve to illustrate this virtue: ozonides; isoprene and caoutchouc; the Walden inversion; desmotropism of acetoacetic ethyl ester; triphenylmethyl and tribiphenylmethyl; thioindigo; salvarsan and neosalvarsan, azomethane; univalent nitrogen in the Hofmann-Beckmann reactions; glycerol mononitrate and glycerol dinitrate, etc., etc.

In the chapter on carbohydrates, the author has taken great pains to simplify the subject matter to bring it within the scope of an elementary presentation. But, at the same time, he has been compelled to discuss relationships which are purely stereochemical in nature. It is hard to understand how these relations can be made clear to the student without the use of the formulas commonly employed to designate space-configurations, when at every turn in the discussion the language teems with phrases which become significant only when considered in conjunction with such formulas. But these formulas are not to be found within the confines of the book. A similar criticism may be applied to other sections of the book which appear to be too advanced for an elementary student and too elementary for an advanced student.

It is probably as unnecessary to say more in a review of this book as it would be to deliver a lengthy address in introducing a speaker well known to his audience.

LAUDER W. JONES.

An Introduction to the Study of Organic Chemistry. By H. F. CLARKE. London: Longmans, Green and Co., 1914. Pp. viii + 484-8°. Price, \$2.00 net.

The keynote of this new text has been sounded at the very beginning in the Preface. The author says:

"In the writing of text books of organic chemistry, there are two distinct and incompatible systems. In the one, it is the practical aspect of the science which is kept in chief view; in the other, the symmetry and homogeneity. The one constantly directs attention to details; the other approaches the subject with the desire of displaying its orderly principles and structural unity. The present writer adheres with conviction to the latter method." Again: "No real knowledge of organic chemistry can be acquired without laboratory work; and to supply in a small textbook, covering the entire field, these practical details so that they can be memorized without actual experience, is contrary to the best interest of students."

A prelude of this kind would lead one to expect a fairly straightforward

account of the salient features of the subject without unnecessary digressions, and, at the same time, facts enough to emphasize the "symmetry and homogeneity" of this branch of chemistry. This is exactly what one finds upon reading the book. At times the statements appear a little bold and dogmatic, unrelieved by amplification, but there is always chance for an argument on points of this kind. In an elementary text, is it not better to avoid too much amplifying of subject matter, always keeping as close to the whole truth as possible, rather than to set up entanglements that may thoroughly dishearten a beginner?

As a matter of fact, text-books of elementary Organic Chemistry serve chiefly as syllabi for quizzes and for courses of lectures in which teachers usually have the opportunity and privilege of introducing what they themselves may think desirable for the proper development of the subject. In view of this condition, this new text is suited admirably to serve as a foundation for science courses, and at the same time to give the student a sufficient array of facts to make the book serviceable as a reference book in connection with a laboratory course, which, I take it, the author believes should always accompany the courses of lectures, quizzes, or other formal methods.

LAUDER W. JONES.

THE JOURNAL

OF THE

American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

THE REPRODUCIBILITY OF THE CADMIUM ELECTRODE.

By FREDERICK H. GETMAN AND VERNETTE L. GIBBONS.

Received February 22, 1915.

TABLE OF CONTENTS.—I. Introduction. II. Study of the e. m. f. of spongy cadmium and stick cadmium electrodes—(a) in concentration cells of methyl alcoholic solutions of cadmium iodide; (b) in concentration cells of aqueous solutions of cadmium iodide. III. Measurements of e. m. f. of stick electrodes against a standard electrode. IV. Consideration of the formation of hydriodic acid in the solution or of cadmium hydroxide on the electrodes as possible causes of the observed abnormalities. V. Consideration of allotropy as possible cause of the observed abnormalities. (a) Historical. (b) Evidence from e. m. f. measurements at different temperatures. VI. Formation of crystals on the electrodes and their analysis. VII. Study of other forms of cadmium electrodes. VIII. Evidence for allotropy of cadmium given by photomicrographic study of the various cadmium deposits.

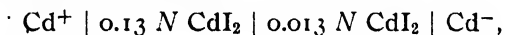
The present work was undertaken to elucidate, if possible, some of the abnormalities observed by Getman¹ in the measurements of the potential of cadmium rods in alcoholic solutions of cadmium iodide. In a study of the reproducibility of the copper electrode, Getman² (in a paper read before a recent meeting of the American Electrochemical Society at Niagara Falls) showed that spongy copper, deposited electrolytically upon a loop of platinum wire, gave a constant and reproducible e. m. f. when measured in concentration cells of aqueous solutions of copper sulfate.

¹ *Am. Chem. J.*, **46**, 117 (1911).

² *Trans. Am. Electrochem. Soc.*, **26**, 67 (1914).

The attempt was first made to study cadmium in the same way. An apparatus was devised similar to the one described by Gibbons and Getman,¹ whereby the two solutions were kept separated from one another except during the time of actual measurement. The measurements were all made at 25°. The temperature was maintained constant to within $\pm 0.05^\circ$, in an electrically controlled thermostat. The purest obtainable methyl alcohol was dehydrated over pure lime for a week, then distilled into a dry receiver which was protected from the gases and moisture in the atmosphere by means of a soda-lime tube. The boiling point of this alcohol was 64.2° to 64.5° at 752 mm. of mercury. The solutions were made up by direct weighing of pure cadmium iodide and all volumetric apparatus used was carefully calibrated. The electrodes were either of spongy cadmium deposited on loops of platinum wire with high current density, or freshly cast rods of the purest cadmium obtainable. The Poggendorff compensation method was employed for measuring the electromotive forces of the different cells, and an enclosed type of Lippmann electrometer was the zero instrument.

The e. m. f. of the combination



with methyl alcohol as solvent was much higher when electrolytically deposited electrodes instead of when stick electrodes were used. The greatest value obtained for any pair of stick electrodes was 0.048 volt, after about five hours' standing in the cell, whereas the greatest value obtained for any pair of electrolytically deposited electrodes was 0.1049 volt, after twenty-four hours' standing. No constant values could be obtained, as in every case there seemed to be an increase in e. m. f. with the time, although there was no regularity in this increase. The cell stood in the thermostat for twenty minutes to acquire a uniform temperature, then the solutions were brought into contact with each other and the first measurement was made as quickly as possible.

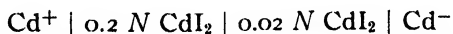
It was thought possible that the greater e. m. f. shown with the electrolytically deposited electrodes might be due to the contact of the finely divided metal with the solution. Therefore, each solution was shaken in a shaking machine for one-half hour in contact with some of the electrolytically deposited metal. The e. m. f. measurements obtained when these solutions were put in the cell were much smaller than before, but quite a deposit of cadmium hydroxide was produced during the shaking. The formation of the hydroxide indicated that the action between the finely divided metal and the methyl alcoholic solution of cadmium iodide was a complex one. It, therefore, seemed inadvisable to consider further the reproducibility of an electrode of cadmium deposited electrolytically with high current density.

¹ THIS JOURNAL, 36, 1645 (1914).

TABLE I.

| Stick electrodes. | | | | | Electrolytically deposited electrodes. | | | | |
|---------------------------|----|------------------------------|----|--------------------|--|----|------------------------------|----|---------------------|
| Total time. Hrs. Mins. | | Diff. in time. Hrs. Mins. | | E. M. F. Volts. | Total time. Hrs. Mins. | | Diff. in time. Hrs. Mins. | | E. M. F. Volts. |
| 0 | 00 | 0 | 00 | 0.0188 | 0 | 00 | 0 | 00 | 0.0181 |
| 0 | 15 | 0 | 15 | 0.0287 | 0 | 15 | 0 | 15 | 0.0264 |
| 0 | 30 | 0 | 15 | 0.0310 | 0 | 30 | 0 | 15 | 0.0366 |
| 0 | 45 | 0 | 15 | 0.0373 | 0 | 45 | 0 | 15 | 0.0477 |
| 1 | 00 | 0 | 15 | 0.0373 | 1 | 00 | 0 | 15 | 0.0530 |
| 1 | 45 | 0 | 45 | 0.0369 | 1 | 15 | 0 | 15 | 0.0599 |
| 2 | 00 | 0 | 15 | 0.0364 | 1 | 30 | 0 | 15 | 0.0623 |
| 2 | 15 | 0 | 15 | 0.0399 | 3 | 15 | 1 | 45 | 0.0773 |
| 2 | 30 | 0 | 15 | 0.0381 | 3 | 30 | 0 | 15 | 0.0792 |
| 2 | 50 | 0 | 20 | 0.0431 | 3 | 45 | 0 | 15 | 0.0792 |
| 3 | 5 | 0 | 15 | 0.0431 | 4 | 00 | 0 | 15 | 0.0792 |
| 3 | 35 | 0 | 30 | 0.0468 | 4 | 15 | 0 | 15 | 0.0812 |
| 4 | 5 | 0 | 30 | 0.0468 | 4 | 35 | 0 | 20 | 0.0814 |
| 4 | 35 | 0 | 30 | 0.0452 | 5 | 40 | 1 | 5 | 0.0841 |
| 5 | 15 | 0 | 40 | 0.0482 | 5 | 55 | 0 | 15 | 0.0857 |
| 5 | 45 | 0 | 30 | 0.0472 | 6 | 10 | 0 | 15 | 0.0867 |
| | | | | | 6 | 25 | 0 | 15 | 0.0871 |
| | | | | | 22 | 45 | 16 | 20 | 0.1018 ¹ |
| | | | | | 23 | 00 | 0 | 15 | 0.1038 |
| | | | | | 23 | 15 | 0 | 15 | 0.1036 |
| | | | | | 23 | 30 | 0 | 15 | 0.1046 |
| | | | | | 23 | 45 | 0 | 15 | 0.1044 |
| | | | | | 24 | 5 | 0 | 20 | 0.1049 |
| | | | | | 24 | 20 | 0 | 15 | 0.1049 |
| | | | | | 24 | 35 | 0 | 15 | 0.1049 |
| | | | | | 24 | 40 | 0 | 5 | 0.1034 ² |
| | | | | | 24 | 55 | 0 | 15 | 0.1046 |

A study of the behavior of stick cadmium electrodes in aqueous solutions of cadmium iodide was then undertaken. The following combination was used:



Three pairs of electrodes were so tested and in each case the e. m. f., at first very small, increased with the time. The electrodes did not seem to be coated with white hydroxide, but, on the contrary, the one in the more concentrated solution became gray in color and appeared coated over with a multitude of tiny crystals; and the electrode in the more dilute solution did not so appear. Evidently the cadmium was deposited upon the positive electrode in a different form from that which dissolved from the negative electrode.

To test this assumption the electrodes were each in turn measured against a standard electrode similar to a calomel electrode, only instead of calomel and 0.1 N potassium chloride, mercurous sulfate and 0.1 N

¹ After standing over night.

² After making a fresh boundary between the solutions.

cadmium sulfate were used. The standard electrode in each case proved to be the positive electrode of the combination:



TABLE II.

| I ₁ . | | | I ₂ . | | |
|--------------------|-------|-------|--------------------|-------|------|
| Total time. | | | Total time. | | |
| Hrs. | Mins. | | Hrs. | Mins. | |
| 0 | 15 | 0 15 | 0 | 00 | 0 00 |
| 0 | 35 | 0 20 | 0 | 20 | 0 20 |
| 1 | 00 | 0 25 | 0 | 40 | 0 20 |
| 1 | 30 | 0 30 | 1 | 00 | 0 20 |
| 2 | 00 | 0 30 | 1 | 20 | 0 20 |
| | | | 1 | 40 | 0 20 |
| | | | 2 | 00 | 0 20 |
| | | | 3 | 15 | 1 15 |
| | | | 3 | 55 | 0 40 |
| | | | 4 | 15 | 0 20 |
| | | | 4 | 35 | 0 20 |
| II ₁ . | | | II ₂ . | | |
| 0 | 00 | 0 00 | 0 | 00 | 0 00 |
| 0 | 20 | 0 20 | 0 | 20 | 0 20 |
| 0 | 40 | 0 20 | 0 | 40 | 0 20 |
| 1 | 00 | 0 20 | 1 | 00 | 0 20 |
| 1 | 20 | 0 20 | 1 | 20 | 0 20 |
| 1 | 40 | 0 20 | 1 | 40 | 0 20 |
| 18 | 5 | 16 25 | 2 | 00 | 0 20 |
| | | | 3 | 10 | 0 20 |
| III ₁ . | | | III ₂ . | | |
| 0 | 00 | 0 00 | 0 | 00 | 0 00 |
| 0 | 20 | 0 20 | 0 | 20 | 0 20 |
| 0 | 40 | 0 20 | 0 | 40 | 0 20 |
| 1 | 00 | 0 20 | 1 | 00 | 0 20 |
| 2 | 25 | 1 25 | 1 | 20 | 0 20 |
| 19 | 15 | 16 50 | 1 | 40 | 0 20 |
| | | | 2 | 00 | 0 20 |
| | | | 3 | 10 | 1 10 |

d.

A freshly cast electrode was measured against the standard electrode.

| | | | | | | | | |
|---|----|------|--------|----|----|----|----|--------|
| 0 | 00 | 0 00 | 1.1231 | 7 | 50 | 1 | 35 | 1.1308 |
| 0 | 20 | 0 20 | 1.1239 | 21 | 50 | 14 | 00 | 1.1308 |
| 1 | 05 | 0 45 | 1.1250 | 22 | 10 | 0 | 20 | 1.1308 |
| 1 | 30 | 0 2 | 1.1254 | 22 | 40 | 0 | 30 | 1.1308 |
| 1 | 55 | 0 25 | 1.1258 | 23 | 10 | 0 | 30 | 1.1309 |
| 4 | 30 | 2 35 | 1.1280 | 24 | 40 | 1 | 30 | 1.1308 |
| 5 | 55 | 1 25 | 1.1292 | 25 | 15 | 0 | 35 | 1.1310 |
| 6 | 15 | 0 20 | 1.1297 | 26 | 15 | 1 | 00 | 1.1310 |

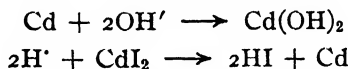
The results are given in Table II. Electrodes which had been used previously as positive electrodes are designated as I₁, II₁, etc., while those used previously as negative electrodes are designated as I₂, II₂, etc.

Another freshly cast electrode gave, when first placed in the cell, an e. m. f. of 1.1237 volts and after 2 hrs. and 40 min. an e. m. f. of 1.1286 volts. This agrees fairly well with the values for corresponding times given in Table II, *d*.

Table II shows clearly that the electrode upon which the gray crystalline layer had been deposited was the stable one and that the electrodes previously used as negative electrodes gradually assumed the constant value of the gray electrodes. The e. m. f. of the cadmium electrode opposed to the standard electrode is seen to be 1.1324 volts (the average of the final values given in Table II, *a*, *b*, *c* and *d*). The difference between this value and the initial value for the freshly cast electrode amounts to 0.0093 volt.

When a solution of cadmium iodide in contact with a cadmium rod was exposed to the air for some time, it became slightly yellowish and, when it was tested with starch paste, a faint blue color confirmed the suspicion that a trace of iodine had been set free.

It was thought possible that the change in the metal and in the solutions might have been caused by small amounts of hydriodic acid, formed as follows:



If such were the case, the solution should show increased conductance, because of the hydrogen ions present, and a coating of cadmium hydroxide upon the metal should be detected by its solubility in ammonium hydroxide.

To decide the question of the formation of hydriodic acid, a highly polished button of cadmium was etched with nitric acid, thoroughly washed and dried. The conductance of 0.2 *N* aqueous cadmium iodide in contact with this button was measured at 25° at intervals over a period of eleven days. There was no increase in conductance and no change in the color of the solution, but there was a marked change in the appearance of the button. The bright crystalline surface became first dull, then black and at last could be seen to have a beautiful growth of shiny black crystals over its entire surface. At the end of two weeks the button was removed, washed, dried and examined microscopically (see page 969).

The buttons of cadmium which had become gray by standing in cadmium iodide or cadmium sulfate solution were tested with ammonium hydroxide solution, but there was no evidence to the eye or under the microscope, that any of the gray substance had been dissolved. An electrode which had stood for three days in 0.2 *N* cadmium iodide solu-

tion, was washed and treated with ammonium hydroxide. The coating apparently did not dissolve and after thorough washing, the electromotive force measurements showed only slight change. Hence the deposit upon the metal was proven not to be cadmium hydroxide.

Samples of the cadmium iodide solution in contact with cadmium did not, however, show the presence of free iodine when air was excluded, although the buttons and rods became gray. The formation of iodine in the solution may, therefore, have been due to oxidation by the air.

The above experiments seemed to indicate that some, if not all, of the abnormalities observed in the measurements of the concentration cells of metallic cadmium in cadmium salt solutions were, most probably, caused by an allotropic change in the metal and that this change was produced when the metal and the salt solution were in contact with each other.

In 1862, Matthiessen and v. Bose¹ mentioned the fact, that cadmium wires became brittle and easily pulverized, when heated several days at 100°. To hold the wires together it was necessary to coat them with varnish. They did not, however, notice any change in the conductivity of the wires.

Cohen and Helderman² have made an extensive investigation of the allotropy of cadmium. Their results are published in three papers and they have shown that cadmium exists in *at least two allotropic modifications and probably more*. One transition point at $64.9^{\circ} \pm 0.1^{\circ}$ has been measured by both pycnometric and dilatometric methods. The former method they consider less reliable, because the density is so easily modified by small amounts of inclusions in the metal. Their study of cadmium amalgams also indicates that there are several modifications of the metal. Cohen and Helderman hold that the electrodes made of cadmium amalgam are in a metastable equilibrium, which may be maintained for years, yet can be changed into stable equilibrium. The explanation given by Cohen for the analogous change from white to gray tin is stated³ as follows:

"Die Erklärung dieser Wirkung dürfte darauf zurückzuführen sein, dass der grauen Form, welche dann die stabile ist, unterhalb des Umwandlungspunktes eine geringere Lösungstension zukommt als der weissen. Infolge der höheren Lösungstension der letzteren wird diese bestrebt sein, in die stabile Form überzugehen; haben sich einmal Spuren von ihr gebildet, so wirken sie beschleunigend auf die weitere Umwandlung."

¹ "Über den Einfluss der Temperatur auf Metalle" 1862.

² I. *Proc. K. Akad. Wetenschappen*, 16, 485 (1913); *Verslag. Akad. Wetenschappen*, 22, 420 (1913); Abstract in *J. Chem. Soc.*, 105-106, II, 52 (1914). II. *Proc. K. Akad. Wetenschappen*, 17, 59 (1914); *Verslag. Akad. Wetenschappen*, Utrecht, 22, 1294 (1914). Abstracts in *J. Chem. Soc.*, 105-106, II, 652 (1914) and in *C. A.*, 8, 2514 (1914). III. *Proc. K. Akad. Wetenschappen*, 17, 122 (1914); *Verslag. Akad. Wetenschappen*, 23, 60 (1914); Abstracts in *J. Chem. Soc.*, 105-106, II, 652 (1914) and in *C. A.*, 8, 3389 (1914).

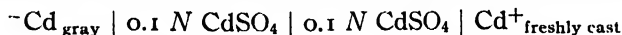
³ Abegg's *Handbuch der Anorg. Chem.*, 3, 550.

Smits,¹ in a paper entitled "Theory of Allotropy as Applied to Electromotive Equilibria," states that the different allotropic modifications give different kinds of ions and the separated metal may be of a different form from that dissolved. He also assumes that salt solutions have an accelerating influence in bringing about a state of equilibrium.

If the salt solution does have an accelerating effect upon the change taking place in the metal, the action of the iodide should be more marked than that of the sulfate. This was found to be the case, for a rod of cadmium became gray much more quickly in a solution of cadmium iodide than in a solution of cadmium sulfate of the same strength. That the temperature also has an effect upon this change was shown, since at a temperature of about 0° the change was more pronounced in a given period of time than it was at room temperature.

If the abnormalities observed in the cadmium concentration cells are due to a transition from one allotropic modification of the metal to another, there should be an electromotive force developed, when a gray cadmium rod and a polished freshly cast cadmium rod are immersed in a solution of a cadmium salt. This electromotive force should be greater the greater the temperature interval above or below the transition point and should undergo a reversal of sign when this temperature is passed, if no other reaction enters in to cause complications. The electromotive force at 25° in a 0.1 *N* cadmium sulfate solution should equal the difference between the electromotive forces of the two electrodes measured against the standard, *i. e.*, 0.0093 volt, and the gray electrode should be the negative terminal of the cell, because of its lower solution tension (see page 958).

To decide these questions, measurements of the electromotive force of the following combination were made at different temperatures:



The gray rods were the ones that had been measured against the standard electrode and had been shown to have a constant electromotive force. The freshly cast rods were polished with emery cloth, thoroughly washed and dried. In every series of measurements the cell was filled with the solution, corked tightly, placed in the thermostat and allowed to stand for one-half hour. At the higher temperatures the cell was opened occasionally to allow for expansion. The solutions were brought into contact with each other, the electrodes inserted in the cell and the first measurement made as quickly as possible. The results of several series of measurements at a given temperature agreed fairly well. The mean values are given in Table III and plotted in Fig. 1.

¹ *Proc. K. Akad. Wetenschappen*, 16, 699 (1913); Abstract in *J. Chem. Soc.*, 105-106, II, 165 (1914).

TABLE III.

| 0.1°. | | | | | 25°. | | | | |
|----------------------------|------------------------------|----|---------------------|--|---------------------------|------------------------------|----|---------------------|---|
| (Average of three series). | | | | | (Average of two series). | | | | |
| Total time. Hrs. Mins. | Diff. in time. Hrs. Mins. | | E. M. F. Volts. | | Total time. Hrs. Mins. | Diff. in time. Hrs. Mins. | | E. M. F. Volts. | |
| 0 00 | 0 | 00 | 0.0362 | | 0 00 | 0 | 00 | 0.0108 | |
| 0 20 | 0 | 20 | 0.0294 | | 0 10 | 0 | 10 | 0.0098 | |
| 0 50 | 0 | 30 | 0.0203 | | 0 20 | 0 | 10 | 0.0096 | |
| 1 20 | 0 | 30 | 0.0181 | | 0 30 | 0 | 10 | 0.0093 | |
| 1 45 | 0 | 25 | 0.0170 | | 0 40 | 0 | 10 | 0.0089 | |
| 2 15 | 0 | 30 | 0.0152 | | 0 55 | 0 | 15 | 0.0086 | |
| 2 35 | 0 | 20 | 0.0144 | | 1 25 | 0 | 30 | 0.0080 | |
| 3 5 | 0 | 30 | 0.0140 | | 1 55 | 0 | 30 | 0.0079 | |
| 3 20 | 0 | 15 | 0.0138 | | 2 25 | 0 | 30 | 0.0076 | |
| 4 20 | 1 | 00 | 0.0131 | | 3 15 | 0 | 50 | 0.0073 | |
| 5 20 | 1 | 00 | 0.0126 | | 3 40 | 0 | 25 | 0.0072 | |
| 6 20 | 1 | 00 | 0.0124 | | 9 30 | 5 | 50 | 0.0055 ¹ | |
| 7 20 | 1 | 00 | 0.0118 ² | | 22 25 | 12 | 55 | 0.0029 ¹ | |
| 8 20 | 1 | 00 | 0.0109 ² | | 23 50 | 1 | 25 | 0.0030 ¹ | |
| 10 00 | 1 | 40 | 0.0099 | | | | | | |
| 20 00 | 10 | 00 | 0.0058 | | | | | | |
| 21 40 | 1 | 40 | 0.0058 ² | | | | | | |
| 25 00 | 3 | 20 | 0.0058 | | | | | | |
| 40°. | | | | | 79.5°. | | | | |
| (Average of three series). | | | | | | | | | |
| Total time. Hrs. Mins. | Diff. in time. Hrs. Mins. | | E. M. F. Volts. | | Total time. Hrs. Mins. | Diff. in time. Hrs. Mins. | | E. M. F. Volts. | |
| 0 10 | 0 | 10 | 0.0100 | | 0 00 | 0 | 00 | —0.0030 | 5 |
| 0 25 | 0 | 25 | 0.0095 | | 0 15 | 0 | 15 | —0.0027 | 3 |
| 0 40 | 0 | 15 | 0.0093 | | 0 50 | 0 | 35 | —0.0026 | 3 |
| 0 55 | 0 | 15 | 0.0083 | | 1 10 | 0 | 20 | —0.0022 | 3 |
| 1 10 | 0 | 15 | 0.0072 | | 1 25 | 0 | 15 | —0.0019 | 3 |
| 1 25 | 0 | 15 | 0.0068 | | 1 50 | 0 | 25 | —0.0017 | 3 |
| 1 55 | 0 | 30 | 0.0060 | | 2 10 | 0 | 20 | —0.0011 | 3 |
| 2 25 | 0 | 30 | 0.0053 | | 3 15 | 1 | 5 | —0.0003 | 2 |
| 2 55 | 0 | 30 | 0.0049 | | 3 50 | 0 | 35 | +0.0007 | 2 |
| 3 15 | 0 | 20 | 0.0046 | | 4 20 | 0 | 30 | +0.0013 | 2 |
| 3 45 | 0 | 30 | 0.0043 | | | | | | |
| 4 30 | 0 | 45 | 0.0040 | | | | | | |
| 5 00 | 0 | 30 | 0.0038 | | | | | | |
| 5 30 | 0 | 30 | 0.0036 | | | | | | |
| 17 30 | 12 | 00 | 0.0032 | | | | | | |

From Table III and Fig. 1 it is seen (1) that there is a progressive change in the e. m. f. of the concentration cells with the time, each curve tending toward a minimum, (2) that the e. m. f. diminishes with increase of temperature, (3) that at 25°, one-half hour after the electrodes are inserted in the cell, the e. m. f. is 0.0093 volt as calculated on page 957, (4) that the gray electrode is the negative terminal of the cell as was to be expected, and (5) that at 79.5°, a temperature above the transition point (64.9°)

¹ From one series of measurements only.

² Interpolated from the curves of the three series.

there is a reversal of the sign of the e. m. f. In the experiments at 79.5° the positive electrode was found to be coated over with white hydroxide of cadmium, which might easily account for the change from a negative

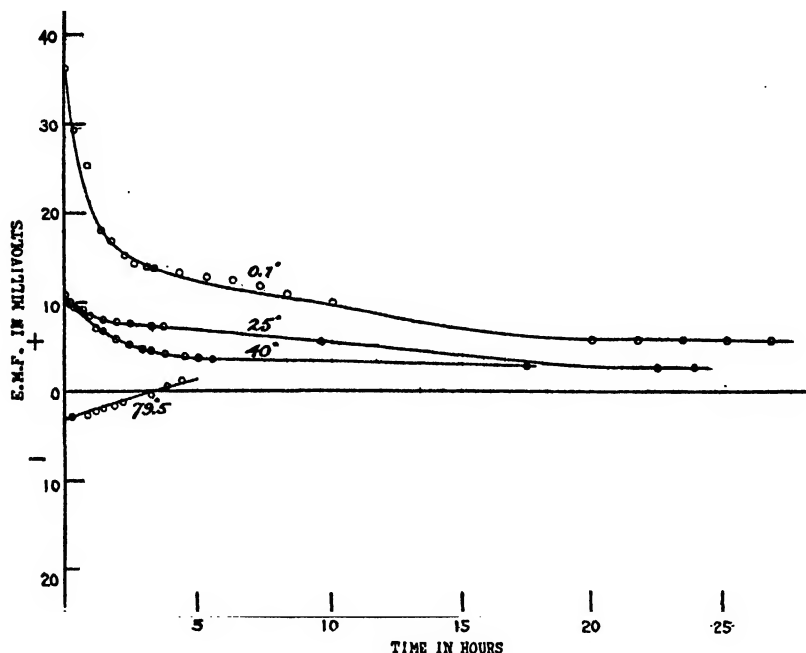


Fig. 1.

to a positive e. m. f. at the close of the series. An attempt was made to carry out a series of measurements of the e. m. f. of the combination at 98° , but the formation of the hydroxide took place so quickly that it was found quite impossible to obtain any reliable values.

Two freshly cast and polished electrodes were then measured against each other in a $0.1\ N$ cadmium sulfate solution. The e. m. f. was appreciable, but fluctuated and the value seemed in some way to depend upon the degree of polishing of the electrode. This behavior might have been expected for the anomalous changes in the potential of cadmium are well known. Thus, Desch¹ makes the following statement: "Cadmium is so sensitive that merely rubbing the surface with emery paper is sufficient to make that specimen the anode when compared with an untreated specimen." The electrodes were washed, dried and left standing over night. They were then polished, washed and dried and placed in fresh $0.1\ N$ cadmium sulfate solution and the e. m. f. of the combination was again determined with the same result as before.

¹ Desch's *Metallography*, p. 287.

The electrodes were then polished and placed in 0.2 *N* cadmium iodide solution and left to stand twenty-two hours in the ice chest, then two hours in the air at about -9° , when the solution solidified. The frozen solution was allowed to melt at room temperature and to stand for two and three-quarters hours before the electrodes were removed, washed and dried. They then appeared grayish and when placed in 0.1 *N* cadmium sulfate solution gave no measurable e. m. f. even after 40 mins. standing. The electrodes were again placed in 0.2 *N* cadmium iodide solution and, after twenty-four hours at room temperature, beautiful metallic crystals were found to be scattered over the gray background. The crystals were examined under the microscope and photographed (see page 966).

Some of the crystals were carefully removed from the electrode with a scalpel. They were found to be very slowly soluble in hydrochloric acid but readily and completely soluble in nitric acid. A few of the crystals were transferred to an evaporating dish, dissolved in a small amount of dilute nitric acid and the solution evaporated to dryness. The residue was dissolved in a small amount of distilled water and analyzed qualitatively. The crystals were found to be pure cadmium.

It seemed advisable to examine the crystalline deposit of cadmium formed upon cadmium or platinum by electrolysis of a cadmium sulfate solution with low current density. The solution employed was made up by diluting 10 cc. of saturated cadmium sulfate solution with 75 cc. of distilled water and 2 drops of dilute sulfuric acid. A current of $N.D._{100} = 0.15$ amperes (approx.) and at an e. m. f. of 2 volts was passed for about 5 hours. The cathode was either a polished, freshly cast rod of cadmium, or a platinum plate sealed into a glass tube. Three crystalline cadmium rod electrodes and one crystalline cadmium plated platinum electrode were so prepared and the e. m. f. of each measured against the standard electrode. The plated cadmium rods gave constant e. m. f. in each case after about 30 minutes in the cell and remained practically constant for at least 22 hours. The values agreed fairly well and were as follows: (1) 1.1343 volts, (2) 1.1336 volts, (3) 1.1340 volts. The cadmium plated platinum electrode showed greater fluctuations between the limits 1.1333 volts and 1.1348 volts over a period of 23 hours.

From the above it is seen that the e. m. f. of these crystalline electrodes is from 1 to 2 millivolts higher than the e. m. f. (1.1324 volts) of the gray crystalline electrodes formed by immersing the freshly cast rods in a solution of cadmium iodide.

The crystalline deposits were examined under the microscope and the crystal forms were in all cases similar to those shown in Fig. 11.

A gray deposit was formed upon the cadmium rod by electrolysis with high current density and its e. m. f. was measured against the standard

electrode. The measurement showed fluctuations between the limits 1.1341 volts and 1.1364 volts over a period of 24 hours.

The effect of amalgamation of a cadmium electrode was studied by measuring its e. m. f. against the standard electrode. There was much variation in the results, no two electrodes gave even approximately the same results in a given time and the values were in all cases much smaller than the similar measurements of the e. m. f. of the crystalline electrodes.

It seems, therefore, that cadmium electrodes reproducible to within 1 or 2 millivolts, when measured against the standard electrode, may be obtained either by allowing a polished cadmium rod to stand in a cadmium salt solution until it has acquired a uniform gray coating, or by electrolytically depositing crystalline cadmium upon a polished cadmium rod with a low current density. The electromotive behavior of cadmium in alcoholic solution of cadmium salts is now being investigated in this laboratory.

Frequent examination of the electrodes with a pocket lens made it apparent that valuable information as to the nature of the change which occurs when cadmium is immersed in solutions of its salts could be obtained by systematic microscopic observations.

Soon after entering upon the microscopic study of the surfaces of the electrode, it became evident that the cylindrical form of these electrodes was not suited to examination with high power objectives. To overcome this difficulty a cylinder of pure cadmium $1\frac{1}{2}$ cm. in diameter and about 3 cm. in length was prepared by casting the metal in a suitable mould. The cylinder was then cut into transverse sections about 4 mm. thick and one surface of each of the resulting buttons was polished. The polishing of the buttons was carried out in the following manner: After smoothing both surfaces of the button with a file, it was mounted with sealing wax in a shallow hole cut in a wooden block and then rubbed on blocks covered with emery paper of regularly graded fineness. Care was taken in changing from one paper to the next finer to rub in a direction at right angles to that previously followed, thus gradually reducing the size of the scratches. After a final abrasion with "cuttle-fish bone paper," the button was rubbed on a piece of velveteen with a jewelry polish to which had been added a few drops of xylol. A final brisk rubbing on a dry piece of velveteen developed a mirror-like surface.

After taking a photomicrograph of the surface of one of these buttons (as shown in Fig. 2) it was immersed in 0.2 *N* solution of cadmium iodide and maintained at a temperature of about 5° by placing in the ice chest. After 15 minutes immersion the button was removed from the solution, successively washed in water, alcohol and ether and then re-examined under the microscope. Unmistakable evidence of a distinct change in the character of the surface was obtained. The button was then replaced

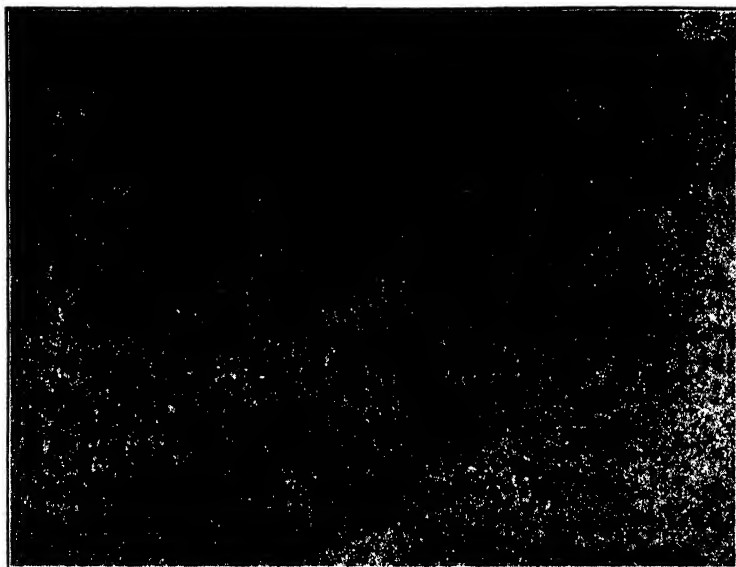


Fig. 2.—Magnification 100.

in the cadmium iodide solution and after 3 hours' immersion was again re-examined microscopically. The small initial nuclei observed after 15 minutes immersion were found to have developed into the well de-



Fig. 3.—Magnification 100.

finer spots shown in Fig. 3. The button was regularly examined at 3 hour intervals, until after 18 hours' immersion the surface had assumed the appearance shown in Fig. 4. In order to determine whether this change



Fig. 4.—Magnification 100.

might be due to a deposition of cadmium hydroxide, the button was immersed for 10 minutes in dilute ammonium hydroxide, and then, after washing with water, alcohol and ether, it was re-examined under the microscope. The appearance of the surface remained unaltered and it was assumed that the deposit was not due to a film of cadmium hydroxide. After two weeks' immersion in 0.2 *N* cadmium iodide solution, the deposit



Fig. 5.—Magnification 200.



Fig. 6.—Magnification 100.

on the button had assumed a distinctly crystalline appearance as shown in Fig. 5. It has already been mentioned (page 962) that well developed crystals visible to the naked eye appeared on two of the electrodes used in the experimental cell, and it seemed of interest to compare these crystals with those observed on the button shown in the preceding illustration. Accordingly, photomicrographs were made of some typical crystals found on the electrodes as shown in Figs. 6 and 7. It was impossible

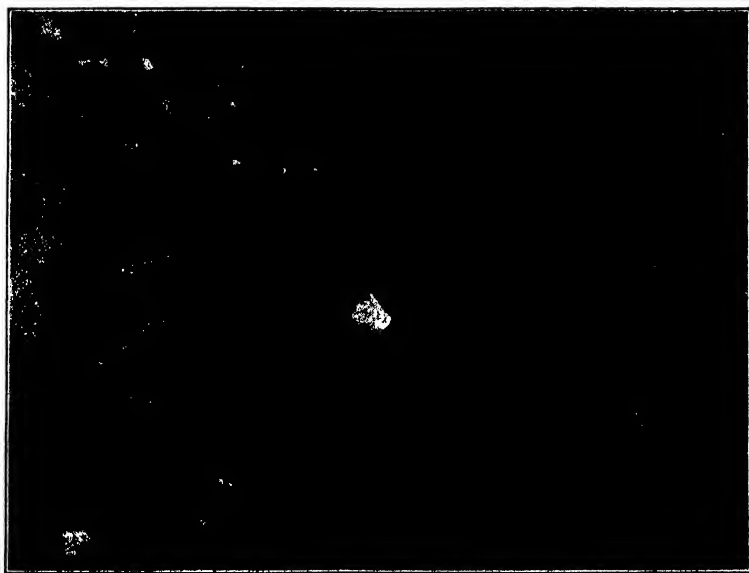


Fig. 7.—Magnification 100.

to bring more than a very limited portion of the field into sharp focus because of the cylindrical form of the electrodes and on account of the thickness of the crystals. However, a careful examination under the microscope in which various portions of the crystals were successively brought into focus, revealed the fact that they belonged to the isometric system, pentagonal dodecahedra and truncated octohedra being the prevailing forms.

Since freshly cast cadmium is known to crystallize in the hexagonal system,¹ the foregoing observations seem to justify the conclusion that prolonged standing in a solution of cadmium iodide involves a change in crystalline form. Furthermore, the change in form being from a system of lower to one of higher symmetry confirms the conclusion drawn from the measurements of electromotive force (page 957) that the freshly cast cadmium electrodes are unstable. In his metallography, Desch² (*Loc.*

¹ Gmelin-Kraut's *Handbuch der Anorg. Chem.*, 4, 109.

² Desch's *Metallography*, "Text-Books of Physical Chemistry," Longmans, Green & Co.

cit) says, "Several metals exist in more than one crystalline modification, in which case the forms stable at high temperatures are of a lower degree of symmetry than those at low temperatures." It has already been pointed out that lowering the temperature favors the formation of a stable cadmium electrode when the metal is immersed in a solution of cadmium iodide.

If the crystalline deposit on the electrode is the stable form of cadmium then it should be possible to inoculate the polished surface of a freshly cast cadmium button with some of these crystals and accelerate the transformation to this modification. In his investigation of the change of white into gray tin, Cohen¹ found that almost complete transformation was effected in 16 days by immersing a specimen of white tin, inoculated with the gray modification, in an alcoholic solution of stannic ammonium chloride. A similar experiment was carried out with a button of cadmium. After making a photomicrograph of the freshly polished surface of the button (Fig. 8) the button was inoculated with several isometric crystals

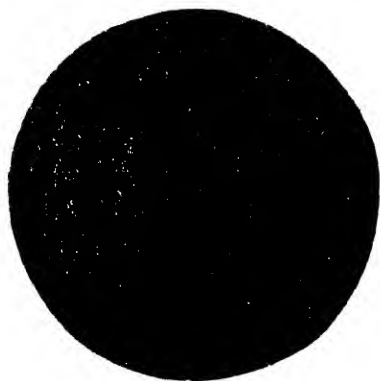


Fig. 8.—Magnification 200.

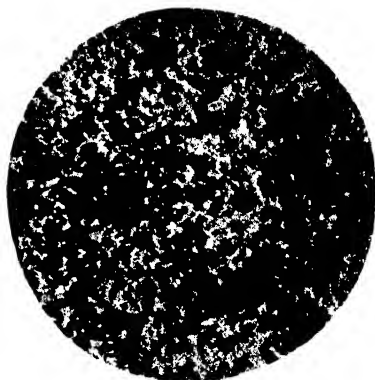


Fig. 9.—Magnification 200.

detached from one of the electrodes and allowed to stand for four weeks in a 0.2 *N* solution of cadmium iodide in ethyl alcohol at about 0°. That a distinct change had occurred is shown in Fig. 9 and that the transformation was more extensive than it would have been had the surface not been inoculated with the stable form of the metal is shown by the photomicrograph (Fig. 10) of an uninoculated polished button treated in exactly the same manner as that shown in Fig. 9. It is evident from this experiment that the transformation from one modification of cadmium to the other is much slower than in the corresponding case of tin.

A microscopic examination of a cadmium electrode upon which cadmium was deposited electrolytically revealed the same general type of crystals as was obtained by prolonged immersion of cadmium rods in a

¹ Abegg's *Handbuch der Anorg. Chem.*, 3, 550.

solution of cadmium iodide, although the potential of the former was about 2 millivolts higher than that of the latter. An experiment was then performed to determine, if possible, whether electrolytically deposited cadmium crystals might not serve as nuclei from which the crystallization would spread to a polished cadmium surface. A polished cadmium



Fig. 10.—Magnification 200.

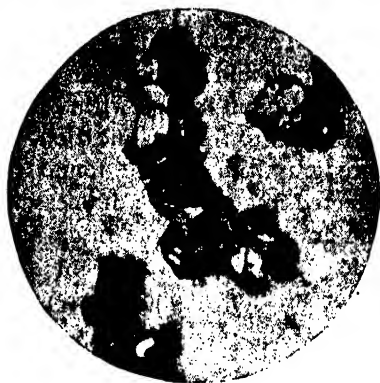


Fig. 11.—Magnification 100.

button was suspended in a dilute solution of cadmium sulfate acidified with sulfuric acid and one-half of the surface of the button coated with a crystalline deposit of electrolytic cadmium ($N.D._{100} = 0.15$ amp., 2 volts). A photomicrograph of the deposit revealed the presence of the crystals shown in Fig. 11. The button was then immersed in 0.2 *N*

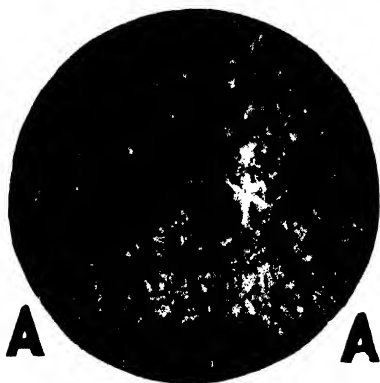


Fig. 12.—Magnification 100.



Fig. 13.—Magnification 100.

cadmium iodide solution and allowed to stand for two weeks at room temperature. At the end of this period the electrolytic deposit and the polished half of the button had acquired a dull gray color. The microscopic appearance of the polished half of the button is shown in Fig. 12, the line of demarcation between the polished portions and that upon

which the cadmium was deposited electrolytically being shown at AA. While a marked crystalline growth is apparent upon the polished half of the button, it is doubtful whether this was accelerated by the presence of the electrolytic deposit.

The etched cadmium button used in the conductance experiments (page 957) was examined microscopically before and after immersion in the cadmium iodide solution. The initial appearance of the button is shown in Fig. 13 and that at the end of two weeks in Fig. 14. These shiny, black crystals appear to belong to the isometric system but the cubic form is apparently predominant. A similar black deposit was obtained upon two cadmium rods, in one case the deposit being distinctly nodular. It seems probable that this is another allotropic modification of cadmium.

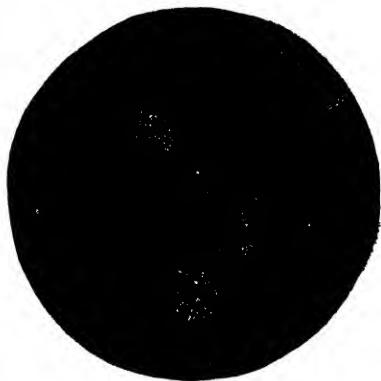


Fig. 14.—Magnification 200.

Newbery¹ considers the dulling or blackening of the surface of metallic electrodes during the passage of a current as due to extremely minute pittings in the metal, as if caused by explosive separation of gas from the interior of the metal. Such, however, was not the case in the present experiments. In every sample of the metal observed under the microscope the change of surface was clearly due to a deposit or growth upon the surface.

The gray form and the bright crystalline forms of cadmium described in this paper have doubtless been obtained by others working on the electrodeposition of cadmium,² but, as far as the authors can learn, the black crystalline form has never been obtained nor have the gray and bright crystalline forms been studied microscopically.

Summary.

1. The measurements of the e. m. f. of concentration cells of methyl alcoholic solutions of cadmium iodide show that neither freshly cast rods of cadmium nor spongy cadmium deposited electrolytically are reproducible.

2. Similarly freshly cast rods of cadmium are shown not to give a reproducible e. m. f. when used as electrodes in aqueous solutions of cadmium iodide.

3. Rods of cadmium which have become gray by standing in cadmium

¹ *J. Chem. Soc.*, 105-106, 2427 (1914).

² "Electrodeposition of Cadmium I," Historical Review, by Mathers and Marble, *Trans. Am. Electrochem. Soc.*, 25, 297 (1914).

iodide solution are shown to give a constant e. m. f. when measured against an unpolarizable electrode. Freshly cast rods of cadmium are shown to attain this value with time.

4. The behavior of cadmium electrodes in concentration cells is explained as due to an allotropic change.

5. Crystalline electrolytic deposits of cadmium on cadmium rods or platinum are shown to give a reproducible e. m. f. when measured against an unpolarizable electrode. This e. m. f. is, however, slightly higher than that given by the gray cadmium electrodes. Amalgamated electrodes are not reproducible.

6. Photomicrographs indicate a change in crystalline form and confirm the conclusions drawn from the e. m. f. measurements.

7. Attempts to inoculate the surface of the freshly cast cadmium with the stable modification indicate that the action is extremely slow.

8. Photomicrographs indicate that in all cases the change is due to a deposit upon the surface instead of to a pitting of the surface.

CHEMICAL LABORATORY, BRYN MAWR COLLEGE,
BRYN MAWR, PA.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE ENTROPY OF VAPORIZATION AS A MEANS OF DISTINGUISHING NORMAL LIQUIDS.

BY JOEL H. HILDEBRAND.
Received February 23, 1915.

In a series of studies which we are making on the theory of solutions, it has become necessary to distinguish between deviations from Raoult's Law, whose cause may be considered physical, and those due to chemical changes. As has been pointed out in a previous paper,¹ the choice between the alternatives in a given case is possible if we know whether or not the pure liquids are associated. For example, the occurrence of vapor pressures greater than those calculated by Raoult's Law in a mixture of benzene and stannic chloride, is explained by Schulze and Hock² on the assumption that the stannic chloride is associated, to a degree depending on the concentration. A great many deviations from Raoult's Law may be explained in this way, as the writer himself has done in the case of a number of amalgams.³ Such an assumption would be unjustifiable if we were sure that both liquids were themselves normal, that is, unassociated, for the presence of another component must tend to diminish such association rather than to increase it. In fact, in the case of benzene

¹ Ermon D. Eastman and Joel H. Hildebrand, "The Vapor Pressure of Gold, Silver and Bismuth Amalgams," *THIS JOURNAL*, **36**, 2020 (1914).

² *Z. physik. Chem.*, **86**, 445 (1914).

³ *Trans. Am. Electrochem. Soc.* **22**, 319, 335 (1912); *THIS JOURNAL*, **35**, 501 (1913); **36**, 2020 (1914).

and stannic chloride, just mentioned, all of the criteria we are able to apply show stannic chloride to be a normal liquid, so that its failure to lower the vapor pressure of benzene to the extent demanded by Raoult's Law is to be explained, not by a reduction in the number of mols of stannic chloride added, but rather to a physical effect such as would result from a change in the internal pressure, tending to increase the escaping tendency of the benzene.

In order to judge similarly of the correctness of the assumptions made in the calculations with amalgams, it is necessary to know whether the liquid metals are normal or associated. Unfortunately, however, most of the relations used to distinguish between normal and associated liquids are applicable only to organic liquids; being additive properties depending upon atomic values determinable only for such elements as form a number of compounds in various proportions. The only relations that are applicable to liquid metals are the surface tension law of Eötvös,¹ and Trouton's rule,² either in its original form or in one of the various modifications that have been proposed.

The application of the former relation to liquid metals has led to the conclusion that they are more or less associated. The value of this testimony will be considered in a future communication, this one being reserved for a discussion of the evidence furnished by the heat of vaporization.

The original Trouton rule states that the heat of vaporization of a liquid, divided by its absolute boiling point, is a constant for all normal liquids. This relation holds very well for normal liquids boiling in the neighborhood of 100° to 300°. It has been derived theoretically from the theorem of corresponding states;³ however, it must hold more closely than this theorem.⁴ As an extreme instance, mercury, for which Trouton's rule holds very well, shows wide deviation from the "law" of corresponding states. Moreover, its critical temperature, though not known, is certainly above 1000°,⁵ so that its boiling point, 632° A, is far from being 0.66 of its critical temperature on the absolute scale, as would be required to give any validity to this proof of Trouton's rule for mercury.

For associated liquids, such as water, alcohol, and liquid ammonia, the ratio is larger, which is explained by assuming that when a liquid is associated and its vapor is not associated, a certain amount of heat is required to dissociate the molecules of the liquid, hence the normal heat of vaporization is increased. The effect on the boiling point is doubtless

¹ *Wied. Ann.*, 27, 448 (1886). See also Ramsay and Shields. *Z. physik chem.*, 12, 431 (1893).

² *Phil. Mag.*, [5] 18, 54 (1884).

³ See for example Irtson, *Z. physik. Chem.*, 53, 633 (1905).

⁴ See Bingham, *THIS JOURNAL*, 28, 717 (1906).

⁵ Menzies, *THIS JOURNAL*, 35, 1065 (1913).

not very large, so that when abnormally high values are obtained the evidence of dissociation seems fairly satisfactory. Since the quotient of the heat of vaporization by the absolute boiling point represents the increase in entropy of the substance during vaporization, and since we wish to refer to this ratio at temperatures other than the boiling point, we will use the less cumbersome term entropy of vaporization.

A rule essentially the same as that of Trouton has been given by Le-Chatelier and Forcrand¹ whereby the entropy of dissociation of certain solid compounds at one atmosphere pressure is approximately 33 calories per degree.

As Trouton's rule has become more completely tested, especially at extreme temperatures, it has become evident that the entropy of vaporization to one atmosphere is by no means constant for all normal substances, but that it increases with the boiling temperature. Various modifications have accordingly been suggested. Two of these have been proposed by Nernst,² *i. e.*, $L/T_b = 8.5 \log T_b$, and $L/T_b = 9.5 \log T_b - 0.007T_b$, where L is the molecular heat of vaporization at constant pressure; and T_b the absolute boiling point. It is impossible to determine from what Nernst says, whether they have any other than an empirical foundation. They seem to be intended chiefly to take into account the low boiling gases. Another formula has been proposed by Bingham,³ $L/T_b = 17 + 0.011 T_b$. This formula is also empirical, and has been constructed without much reference to liquids boiling at very high or very low temperatures. More recently Forcrand⁴ has published a formula, also empirical, but which has attempted to include liquids with very high, as well as those with very low boiling points: $L/T_b = 10.1 \log T_b - 1.5 - 0.009T_b + 0.0000026T_b^2$. The course of this equation at high temperatures was determined by using data for the boiling points of silver and copper. It should be mentioned that the values at high temperatures would be considerably different if the data for zinc, bismuth, lead and tin, apparently as trustworthy as those for silver and copper, had been taken into account. For this reason the use of the formula by Forcrand for extrapolation to still higher temperatures, to get the boiling point of carbon, cannot be regarded as very significant.

Except for zinc and cadmium, the only values for the vapor pressures of metals at high temperatures are those of Greenwood,⁵ who determined the boiling points at three different pressures. Unfortunately, it is not possible to decide how much weight to give to these measurements. The

¹ *Ann. chim. phys.*, [7] 28, 384, 531 (1903).

² *Gött. Nachr.*, 1906.

³ *THIS JOURNAL*, 28, 723 (1906). A recent paper by Sonaglia should be mentioned in this connection, *Nuovo Cimento*, 7, 321 (1914).

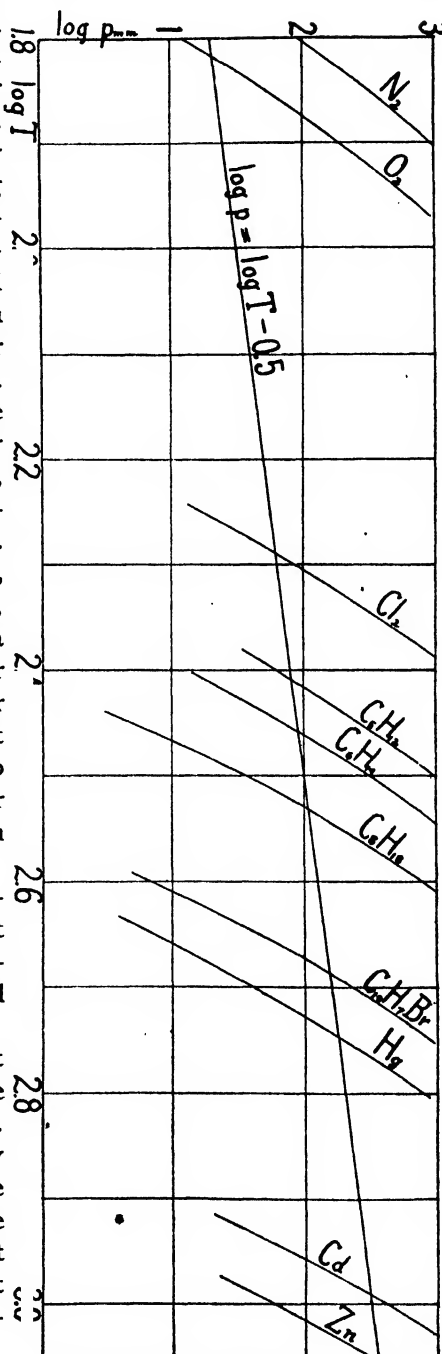
⁴ *Compt. rend.*, 156, 1439, 1648, 1809 (1913).

⁵ *Proc. Roy. Soc. [A]*, 83, 483 (1910).

heat of vaporization calculated from one pair of values is widely different from that calculated from another pair in the case of each element. The simplest way to test vapor pressure measurements is to plot $\log p$ against $1/T$, which should give almost a straight line. The measurements of Barus¹ on cadmium and zinc when plotted in this way seem to be very satisfactory, a number of values being given in each case. On the same basis, however, the data of Greenwood for the other metals can hardly have much weight, either for or against any generalization on the entropy of vaporization. We hardly feel justified, therefore, in using the formula of Forcrand, gotten by using arbitrarily the data for two metals, to decide whether or not several others are normal or associated in the liquid state. It becomes necessary, therefore, to have some more justifiable basis for extrapolation from ordinary to high temperatures.

A formula has been published recently by Cederberg,² but it cannot be applied to the metals, as it requires a knowledge of the critical pressure and temperature.

It must be noted, first of all, that the boiling point at one atmosphere pressure has no special significance. We may, if it is desired, select any pressure or function of the pressure and temperature for comparing the entropy of vaporization of different substances. In order to represent the entropy of vaporization graph-



¹ *Phil. Mag.*, [5] 29, 141 (1890).

² *Z. physik. Chem.*, 77, 498 (1911).

ically we may put the Clapeyron-Clausius equation, $d \ln p / dT = L / RT^2$, into the form: $d \log p / d \log T = L / RT$. If, then, $\log p$ is plotted against $\log T$, the tangent to the resulting curve at any point represents the entropy of vaporization at that temperature divided by R . The appearance of such curves is shown in the accompanying figure, the original scale being greatly reduced in order to represent a number on the same plot. Now, if Trouton's rule in the original form were true, then the tangents to all of these curves should have the same slope at a value of $\log p$ corresponding to one atmosphere. It is evident, however, that this is not the case, but that the slope of the curves, at equal values of $\log p$, increases regularly with the logarithm of the temperature. Therefore, the entropy of vaporization for different substances cannot be the same at equal pressures, but rather at pressures that increase in some way, with the temperature. It was found that the tangents to the curves at points cut by any line of unit slope have the same slope, with a remarkable degree of precision. For accurate comparison the curves can be plotted on different sheets of transparent paper, and a line drawn on each whose equation is $\log p = \log T + K$, where K is a constant. By sliding one plot over the other, keeping this straight line superimposed on the two plots, it is possible to superimpose the curves with surprising accuracy, from the curves for nitrogen and oxygen up to those for cadmium and zinc.

The significance of the line of unit slope is this: since, for any vapor, at pressures low enough for it to obey the gas laws sufficiently accurately, we have the equation $p = RTc$, where c denotes concentration, and therefore $\log p = \log T + \log Rc$, the constant, K , in the above equation must equal $\log Rc$, and therefore along such a line c is constant. Our conclusion may be stated in words as follows: the entropy of vaporization for normal liquids is the same when evaporated to the same concentration, *i. e.*, when the final mean distance between the molecules of vapor is the same.

In Table I are given values of L/RT which make possible a numerical comparison of the new rule with that of Trouton, or its equivalent. The first column of figures contains the values of L/RT_c according to the new rule, the subscript denoting equal concentration of vapor. These values were obtained by plotting $\log p$ (in mm. of mercury) against $\log T$ very carefully on a large scale, and determining the slope of the tangents to the curves when $\log p = \log T - 0.5$, corresponding to a value of c of 0.00507 mols of vapor per liter. The selection of this concentration was entirely arbitrary, there being no apparent reason for choosing any particular concentration except the desirability of avoiding any extrapolation of the experimental data, that is, using a line that would cut all of the curves so plotted. In the second column are the values of L/RT_p , taken from the same curves but at equal values for the pressure, so as to correspond to Trouton's rule. However, instead of comparing the values when the

TABLE I.

| Substance. | L/RT_c $\log p = \log T - 0.5$ | L/RT_p $\log p = 2$ | T_c | T_p |
|---------------------------|-------------------------------------|--------------------------|-------|-------|
| Nitrogen..... | 13.8 | 11.0 | 55 | 63 |
| Oxygen..... | 13.8 | 11.4 | 75 | 81 |
| Chlorine..... | 13.9 | 13.5 | 194 | 200 |
| Pentane..... | 13.5 | 13.2 | 256 | 260 |
| Isopentane..... | 13.7 | 13.5 | 258 | 262 |
| Hexane..... | 13.6 | 13.3 | 286 | 289 |
| Carbon tetrachloride..... | 13.5 | 13.4 | 294 | 295 |
| Benzene..... | 13.7 | 13.7 | 298 | 299 |
| Fluorobenzene..... | 13.7 | 13.7 | 303 | 304 |
| Stannic chloride..... | 13.6 | 13.6 | 329 | 328 |
| Octane..... | 13.8 | 13.9 | 338 | 339 |
| Bromonaphthalene..... | 13.8 | 14.1 | 486 | 472 |
| Mercury..... | 13.1 | 13.5 | 560 | 533 |
| Cadmium..... | 13.2 | 14.8 | 988 | 908 |
| Zinc..... | 13.2 | 15.1 | 1130 | 1030 |
| Ammonia..... | 16.2 | .. | 200 | .. |
| Water..... | 16.0 | .. | 325 | .. |
| Ethyl alcohol..... | 16.7 | .. | 307 | .. |

pressure of the vapor is one atmosphere, and when it may deviate considerably from the gas laws, it was thought fairer to choose a somewhat lower pressure. Accordingly the values in the table are for $\log p = 2.0$, corresponding to a pressure of 100 mm. of mercury. If Trouton's rule holds for one pressure it must hold for any other pressure. In the third and fourth columns are the temperatures at which the values in the first two columns were determined, respectively.¹

The values of L/RT_c are also given for ammonia, water and alcohol, typical associated liquids, in order that the magnitude of the deviation from that cause may be evident.

It will be seen that the deviation of L/RT_c from the mean is scarcely greater than the limit of error except for the metals, for which it is several per cent. less. There is no systematic change with the temperature. On the other hand, the values of L/RT_p at equal vapor pressures, corresponding to Trouton's rule, show a systematic increase from 11.0, for nitrogen, to 15.1, for zinc.

There are two principal deviations from the new relation that should be pointed out. The difference between L/RT_c for the metals and the values for the other substances in the table, while not great, is distinctly

¹ The sources of the vapor pressure data used were as follows: nitrogen, Fischer and Alt, *Ann. Phys.*, [4] 9, 1149 (1902); oxygen, Estreicher and Olszewski, *Phil. Mag.*, [5] 40, 454 (1895); chlorine, Johnson and McIntosh, *THIS JOURNAL*, 31, 1138 (1905); pentane to octane, Young, *Sci. Proc. Roy. Dublin Soc.*, 12, 374 (1910); bromonaphthalene Kahlbaum, *Z. physik. Chem.*, 26, 603 (1898); mercury, Smith and Menzies, *THIS JOURNAL*, 32, 1447 (1910); cadmium and zinc, Barus, *Loc. cit.*

more than the difference due to any uncertainty in the experimental data. It may be suggested that this deviation is due to a difference in molecular complexity. When a molecule escapes from the liquid to the vapor it is relieved of a very high internal pressure which exists in the liquid, and may, conceivably, expand with an absorption of energy. The amount of energy so absorbed we should expect to be greater in the case of molecules containing many atoms than with those containing but few. The expression for the entropy of vaporization might be written, therefore, $(L + e) / RT$, where e denotes the energy absorbed within the molecules on expansion from the high pressures existing within the liquid to the low pressure existing in the vapor. The quantity e is doubtless small compared with L , that is, most of the energy is required to overcome the attraction between the molecules, and but little in the expansion of the molecule itself. It is possibly safe to say, in the light of our rule, that in so far as it concerns the overcoming of attraction between the molecules, the entropy of vaporization to the same concentration is the same for all normal liquids. If a liquid is associated, a third, and much larger quantity of energy is involved in the dissociation of the complex molecules into simpler ones. In such cases the total entropy of vaporization is distinctly greater than the normal value for the given concentration, as is seen in the last three instances in the table.

Another deviation is found in the cases of hydrogen and helium. If the vapor pressure data¹ at these low temperatures can be trusted, then the entropy of vaporization is less than our rule would require, although the agreement is very much better than it is on the basis of the original Trouton rule. The values could not be included in Table I without a wide, and hence uncertain, extrapolation to lower pressures in order to use the same concentration as was used in the table. The direct comparison can be made however, at higher pressures. On putting $\log p = \log T + 0.444$, corresponding to a concentration of 1 mol in 22.4 liters, we obtain the values in the first row of Table II. In the second row are given for comparison the values of L/RT_p , when $\log p = 2.00$, as before.

TABLE II.

| Substance..... | Helium | Hydrogen | Nitrogen | Oxygen |
|----------------|--------|----------|----------|--------|
| L/RT_c | 7.0 | 9.8 | 10.5 | 10.4 |
| L/RT_p | 5.0 | 8.6 | 11.0 | 11.4 |

In view of the rapid change in the specific heats of solids, and presumably also of liquids, in the neighborhood of the absolute zero, and the consequent effect on the heat of vaporization, the deviation from our rule at these low temperatures might perhaps be expected. A further con-

¹ Data for hydrogen, Travers and Jacquerod, *Proc. Roy. Soc.*, 70, 490 (1902); *Z. physik. Chem.*, 45, 416 (1905); data for helium, Onnes, *Versl. K. Akad. Wet. Amst.*, 19, 1194 (1911) *Comm. Physik. Lab. Leid.*, 119.

sideration of the possibility of introducing the specific heats so as to make the necessary correction will be postponed till later.

It is possible to express the rule here given in the form of an equation which gives the vapor pressure of any normal liquid at any temperature in terms of some other such liquid chosen as standard. Let us consider the vapor pressures of two normal liquids, one of which we will take as a standard for the reference of all others. We may integrate the Clausius equation for each of these liquids, assuming, for the moment, for the sake of simplicity, that the heat of vaporization does not vary with the temperature. The resulting equations for the two substances are then:

$$\ln p = -L/RT + I \quad (1)$$

$$\ln p_s = -L_s/RT + I_s \quad (2)$$

the subscript referring to the one chosen as standard. Since $p = RTc$, we can write

$$\ln c + \ln R + \ln T = -L/RT + I \quad (3)$$

$$\ln c_s + \ln R + \ln T = -L_s/RT + I_s. \quad (4)$$

Let us now select temperatures, T_c and $T_{c,s}$, at which the concentration of the vapor will be the same for the two substances, *i. e.*, $c = c_s$, when, according to our principle,

$$L/RT_c = L_s/RT_{c,s}. \quad (5)$$

We may then subtract Equation 4 from Equation 3, obtaining

$$\ln T_c - \ln T_{c,s} = I - I_s. \quad (6)$$

Let us call

$$T_c/T_{c,s} = a, \quad (7)$$

whence

$$L = aL_s \quad (8)$$

and

$$I - I_s = \ln a. \quad (9)$$

We are thus able to calculate L and I for any substance from the corresponding values for the standard substance using a single constant, a , so that this constant becomes the sole characteristic of a normal liquid necessary to define its vapor pressure with considerable accuracy. We may write, then, a universal vapor pressure law for such liquids by substituting for L and I , in Equation 1, the values given by Equations 8 and 9, obtaining the equation

$$\ln p = -aL_s/RT + I_s + \ln a. \quad (10)$$

It must be recognized, of course, that this equation does not take account of the change of the heat of vaporization with the temperature, and hence cannot be an exact equation. However, the change in the heat of vaporization depending on the difference between the specific heats of vapor and liquid, is not large, and is not very different for various liquids, so that Equation 10 becomes more exact if written

$$\ln p = -a/R \int L_s/T \, dT + I_s + \ln a, \quad (11)$$

where L_s is a function of the temperature.

This equation gives another method of plotting vapor pressure data so as to distinguish normal from associated liquids. Equation 11 may be put in the form

$$\frac{\log p/a}{T/a} = \frac{1}{2.3 R} \int L_s dT + I_s. \quad (12)$$

The right hand member of this equation is common to all normal liquids, so that the curves for all normal liquids can be superimposed by plotting $\log bp$ against bT , where $b = 1/a$. These curves are nearly straight lines, so that they are convenient for testing the accuracy of the experimental data and for comparing different substances with each other. The curves for associated liquids cannot be made to coincide with those for unassociated liquids by this means, but will be steeper, due to higher values for the heat of vaporization.

It should be noted that Equation 9, $I - I_s = \ln a$, gives the relation between the integration constants of the Clausius equation for all normal liquids, the "chemical constants" of Nernst, which have received considerable attention from him and others.

The question mentioned at the beginning of this paper, and which suggested the present study, regarding the association of liquid metals, cannot be answered very fully from the experimental data at hand. Mercury appears in the light of a perfectly normal liquid, the slight deviation being opposite in direction to that which indicates association, and being explainable on the basis of a smaller latent heat of expansion of the molecules themselves. Zinc and cadmium likewise appear normal at the temperatures in question. They might, however, be associated at much lower temperatures, such as were used in the amalgam measurements. This possibility could be excluded only by careful measurements at very low vapor pressures.

Summary.

It has been found that the entropy of vaporization (*i. e.*, the molecular heat of vaporization divided by the absolute temperature at which vaporization takes place) is the same for all normal liquids, not, as in Trouton's rule, where the vaporization takes place at the same pressure (one atmosphere), but when it takes place at the same concentration of vapor.

This fact may be expressed in the form of a vapor pressure equation containing a single constant characteristic of the liquid, this constant being determined from the temperatures necessary to give the same concentration of vapor in the different cases.

[FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF LIVERPOOL.]

A THEORY OF CHEMICAL REACTION AND REACTIVITY.

By E. C. C. BALY.

Received February 12, 1915.

During the last ten years a great number of papers have been published describing the absorption spectra of organic compounds, and the majority of these publications have dealt with the constitution of these compounds, the assumption being made that there exists a definite correlation between the primary structure of the molecule and the type of light absorption which it exerts. One of the oldest theories of constitution is the quinonoid theory, which categorically attributes visible color to compounds which possess a constitution analogous to that of ordinary benzoquinone. It is hardly necessary to point out the danger that attends the use of a physiological sensation of color as a criterion of constitution in this connection. There often exist pairs of compounds which to the eye have exactly the same color and yet when their absorptive power towards light is spectroscopically examined it is found that the compounds are materially different. As a matter of fact the application of accurate spectroscopic methods to the problem very soon revealed considerable difficulties and proved that the quinonoid theory is by no means as secure on its foundations as had previously been supposed. Some of these difficulties have been recognized by Hantzsch, who has put forward theories which differ to a certain extent from the old quinonoid theory. Hantzsch, however, still maintains that there is a definite correlation between light absorption and structure, and when he succeeded in preparing five differently colored alkali metal salts from one colorless acid he attributed essentially different formulas to them all.¹ But it was not long before Hantzsch also found himself in difficulties, because after he had obtained a number of different modifications of *m*-nitroaniline he was obliged to confess that there are not enough different formulas to go round.² It is not necessary here to specify the essential points of Hantzsch's theories and sufficient has already been said to indicate that the fundamental basis of them, and the older (quinonoid) theory, is the assumption of the existence of an absorption structure correlation. It may be pointed out, however, that there is not one particle of evidence to show why any one of the structural formulas devised by Hantzsch should possess a color different from that of any other. Indeed, recent investigations into the problem of light absorption by organic compounds by no means favor the view that there is any direct relation between absorption and constitution, if such relation is held to mean that when a colored salt is obtained from a colorless acid or base the parent substance

¹ Hantzsch, *Ber.*, 42, 966 (1909); Hantzsch and Robison, *Ibid.*, 43, 45 (1910).² *Ber.*, 43, 1662 (1910).

has changed its constitution in the salt. The principal outcome of this work is the establishment of a definite relation between light absorption and chemical reactivity. The evidence obtained is so strong that it is necessary to formulate a new theory to account for the observed phenomena, a theory which must at the same time embrace all those experimental facts which appear to support the color constitution relation. It is proposed in this paper to develop this theory from the chemical side, and only briefly to indicate its bearing upon the problems of light absorption.

It follows from the Zeeman effect, that is to say, the resolution of spectrum lines into doublets, triplets, etc., in a powerful magnetic field, that the particles or atoms producing these lines must possess magnetic fields of their own. In a paper dealing with the pressure shift of spectrum lines, Humphreys¹ discusses these atomic fields and shows that they are capable of explaining the phenomena of the Zeeman effect and also of the shift of spectrum lines under the influence of pressure. While these atomic fields have been taken into consideration in explaining such physical phenomena as the above, their influence upon the properties of molecules does not seem to have received notice. These fields must possess both a polar and a quantity factor, and it would follow that atoms which are markedly different in their chemical properties must differ markedly in the polar factor of their force fields. When two such atoms approach one another sufficiently closely, the force lines due to their respective force fields will tend to condense together with loss of energy and with the formation of a condensed field. A potential gradient will thus be set up and it seems possible that if this gradient be sufficiently steep a transference of one or more electrons will take place from one atom to the other, whereby a true chemical compound of the two will be established. Primary valency would thus only mean the transference of one or more electrons along the potential gradient which is set up by the condensing together of the force lines arising from the electromagnetic fields of two atoms of opposite type that are brought close together. On these lines, therefore, it may be said that the chemical reaction or combination between the two atoms is due in the first instance to the force fields appertaining to the two atoms.

Turning now to the compound that is produced, it is evident that the general stability will depend upon the condensed force field between the two atoms. Before such a compound can be decomposed or resolved into its elements this force field must be opened up, and, therefore, the greater the number of force lines that are condensed within the field the more stable will be the compound and the greater the amount of energy required to decompose it.

¹ *Astrophys. J.*, 23, 233 (1906).

In the general case of any molecule it is clear that the independent existence of the several force fields due to the atoms composing the molecule must represent a metastable condition. A certain amount of condensation of the force lines of the various force fields must take place with the escape of energy and the establishment of a closed molecular force field which will determine the properties of the molecule. If a molecule of one compound reacts with a molecule of another compound such reaction takes place by virtue of their respective force fields. If these fields are of opposite type the force lines of the two will condense together with the result that an addition compound of the two is formed. Just as in the case of the two atoms dealt with above, this addition compound will possess potential gradients and if these be sufficiently steep there will follow a transference of one or more electrons between the constituent atoms with the formation of new chemical individuals.

Perhaps an example will make this more clear, but in quoting such an example it must be remembered that reactions which take place by means of ions are for the moment excluded for reasons that will presently be made clear. We may take a perfectly general case of an acid HX and a base YOH . According to the present theory the first stage of the reaction will be the formation of the addition compound YOH, HX , arising from the condensing together of the force lines of the molecular fields of YOH and HX . Within this complex a potential gradient will exist and if this is steep enough the electrons will rearrange themselves with the formation of XY, H_2O . Another way of stating the same fact is to say that the change within the complex will take place if the system XY, H_2O has less energy than the system YOH, HX . If it has less energy, then a new chemical individual XY is formed and we say that a chemical reaction has taken place.

A very important fact may be noticed here in passing, namely, that a chemical reaction will only occur when the gradient within the complex first formed is sufficiently steep to cause the electrons to migrate. The complex between the two original molecules will of course be formed whether or no a true chemical reaction occurs, for the formation of the complex depends only upon the force fields of the two molecules that are brought together. In this way we are enabled to recognize a very large gradation between the condition when a chemical reaction occurs between two molecules and the condition when, owing to their force fields being exactly the same, the molecules have no mutual influence whatsoever. This recognition of mutual influence between two molecules when no specific chemical reaction occurs is of great importance both in pure chemistry and in the phenomenon of light absorption.

According to the above view the reaction between molecules depends upon their force fields. But it has been already shown that these force

fields normally must be more or less closed, according to the measure of the polar and quantity factors of the several fields of the constituent atoms. The reactivity of any molecule must vary inversely as its force field is closed. If, owing to the inherent properties of the atomic fields, the force lines can form a completely closed system, then the molecule will possess no reactivity. If two such molecules with completely closed fields are brought together it is evident that they can have no influence upon one another, and, further, this absence of influence will be entirely independent of what their chemical properties in solution would lead us to expect. It would seem that in this fact is to be found the explanation of the absence of any reaction between HCl and NH_3 , 2H_2 and O_2 , 2CO and O_2 , etc., in the complete absence of water. The first case is peculiarly interesting since the known acidic and basic properties of these two gases would at once lead us to expect that they should immediately combine to form NH_4Cl . The other cases mentioned might be criticised from the point of view that in each of them the molecules of at least one diatomic gas have to be resolved into atoms before the chemical reaction can proceed. The HCl and NH_3 reaction is free from that possible objection, for it is purely one of addition, and yet it does not take place if the gases are dry. According to the present theory the reason why these two gases do not combine together lies in the fact that the molecules of both possess completely closed force fields and, therefore, they can have no influence upon one another. An exactly similar explanation holds good for the converse case, namely, that NH_4Cl vapor does not, when dry, dissociate into HCl and NH_3 . The molecules of NH_4Cl must possess a completely closed field which is not readily opened up and, therefore, when the substance is converted into vapor the molecules do not dissociate.

On the other hand, although a certain amount of condensing together of the force lines due to the atomic fields must occur *ex hypothesi*, yet by no means must the resulting force fields always be entirely closed. When the maximum possible condensing together of the force lines has occurred with the maximum possible escape of energy, there may be left over an uncompensated balance of force lines. This residuum will determine the properties of the given molecules and will give rise to what has long been recognized by chemists as residual affinity. Although this residual affinity has proved itself a very useful friend to chemists, yet it has always been of a somewhat mysterious, not to say mystic, nature which in moments of doubt as to the true dogma has from time to time been invoked to play the role of a *deus ex machina* and relieve the exigencies of the situation.

On the present theory, the whole of the reactivity and chemical properties of atoms and molecules is due to the force fields which have been proved to exist in the immediate neighborhood of the atoms. Chemical union

between atoms, chemical reaction between molecules, both are due to these force fields, and valency itself would seem not to be the *causa causans* of such reactions but to be a resultant effect. Valency in its stoichiometrical meaning is due to the interatomic rearrangement of the electrons when the potential gradients within the addition complexes first formed are sufficiently steep and the electronic transference results in a smaller energy content of the product. The so-called residual affinity is the uncompensated residuum when the maximum possible condensation of the force lines of the molecule has taken place. When this residuum is vanishingly small the given molecule exhibits no evidences of chemical reactivity, but when, as is more usually the case, the residuum has a finite value the molecule does possess an observable and measurable reactivity.

Among chemical compounds which possess a balance of uncompensated force lines or residual affinity water may be mentioned as a very typical example. The extraordinary power possessed by water of forming addition complexes with other molecules is too well known to need emphasizing here, but one or two points in connection with the hydrating power of water may be described. In the first place Humphreys, in his paper referred to above, showed that one of the results of the existence of the electromagnetic fields is the tendency of the mutually attracting faces of the atoms to be brought near together, and of the mutually repelling faces to be kept comparatively far apart. When, therefore, a molecule of a salt hydrates itself, owing to the formation of a closed force field between water and salt molecules, it is obvious that the distribution of the molecules must be symmetrical. Barlow and Pope¹ have shown that in such cases as $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3\cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ the addition of the water molecules takes place entirely along one axial direction of the crystal, that is to say, only one axis of the crystal grows on hydration. This, as readily can be seen, is an absolutely necessary sequitur from Humphreys' deduction. Indeed, it would seem that the conception of electromagnetic force fields gives a complete and rational explanation of all Barlow and Pope's observations, but this cannot be entered into here.

Again, the question of the hydrolysis of salts may be considered in connection with the present theory. When a salt hydrates itself there is formed a complex field due to the condensing together of the force lines of the two components, salt and water. In this complex there are two gradients to be considered, one between the component atoms of the salt and the other between the salt and the water. As long as the former is very steep, as it is in the case of the salts of strong acids and bases, then the tendency to hydrolyze will be a minimum. If, how-

¹ *J. Chem. Soc.*, 89, 1675 (1906).

ever, the former gradient is shallow, the gradients between the salt and water become relatively steeper. In such a case a rearrangement of the electrons will occur with the formation of acid and base from salt and water. The hydrolysis of a salt has been taken as a typical example of a chemical reaction, for it shows the rationale of the phenomena on the lines of the present theory.

From what has already been said, it is obvious that if the closed force field of a molecule be opened or unlocked its reactivity will be enhanced. This unlocking may be brought about in two ways, namely, by the use of a substance possessing residual affinity or by the action of light. If the molecules of a compound, the force fields of which are closed, be brought into the neighborhood of the molecules of another compound possessing residual affinity the force lines of the latter will interpenetrate the closed fields of the former, with the result that they will be opened and endowed with enhanced reactivity. The simplest case to consider is that of the solution of the closed force-field molecules in a solvent possessing residual affinity. The free force lines of the solvent molecules will interpenetrate the closed fields of the solute molecules, with the result that these will now be capable of reacting with any other suitable substance dissolved in the same solvent. Clearly, however, the case is an absolutely general one. The tendency of molecules possessing residual affinity will always be to open up the closed fields of other molecules whenever the two molecular types are brought together, whether an actual solution is formed or not, with the result that the previously closed fields become endowed with reactivity. The bearing of this upon chemical phenomena may be considered from three points of view.

In the first place the enhancement of the reactivity of the substance brings us at once to catalysis and indeed gives us an explanation of this phenomenon. Catalysis may be looked upon as the enhancement of the reactivity of one or more of the components of a reaction and a catalytic agent is a substance which, from the nature of its residual affinity, has the power of opening up the closed fields of the reactant molecules to a greater extent than they otherwise would be under the prevailing conditions. Conversely a negative catalyst is an agent which has the power of closing the force fields to a greater extent than they otherwise would be. Some advantage is held by this theory of catalysis because it gives a rational explanation of the positive and negative effects without the somewhat cumbersome conception involved in the ordinary theory of negative catalysis, namely, that a negative catalyst is one which destroys a positive catalyst assumed previously to be present.

A second point arises when the difference in type is considered of the force fields of the two groups of molecules, solute and solvent. It is clear that if the solute possesses basic characteristics the most suitable

solvent for the purpose of opening it up will be one the residual affinity of which is acid in type, and, conversely, a solute of acid type will most readily be opened up by a basic solvent. On the other hand, a solute the force field of which is not pronouncedly basic or acid will tend to be opened both by an acid and by a basic solvent, but the manner in which the opening up takes place will be different in the two cases. The potential gradients existing within the closed system of the solute will be attacked differently by the force lines of a basic and of an acid solvent. This will result in a difference between the reactivity of the solute in the two cases and, indeed, the solute will present amphoteric properties. An amphoteric substance, on the present theory, is to be defined as one the closed field of which is opened in a different manner by a basic and an acid solvent. A typical example of an inorganic amphoteric compound is aluminium hydroxide, the reactivity of which is different in acid and basic solvents, while an example of an organic amphoteric compound is nitrobenzene, the force field of which is opened quite differently by sulfuric acid and by dimethylaniline.

A third aspect of the opening-up process concerns the case when the solute possesses at least one steep potential gradient, and the residual affinity of the solvent differs markedly from that of the two atoms of the solute between which the potential gradient exists. Such cases as this occur more particularly in inorganic chemistry with the acids, bases, and salts. If the opening-up process be carried to the farthest possible extent the logical consequence will be the complete resolution of the solute molecule into two entities, each of which will be fully solvated owing to the new conditions under which the force lines have formed condensed systems with those of the solvent. As a result of the existence of the potential gradient in the original molecule one or more electrons will have migrated from one atom to the other, and, therefore, the two entities formed by the complete resolution of the closed field of the solute molecule will carry equal and opposite charges of electricity. Ionic dissociation, therefore, is a logical sequence of the force-field theory. The theory, however, gives a different perspective of chemical reaction and reactivity from that presented by the ionic dissociation hypothesis. Whereas the latter attributes all chemical reactions between dissociated salts to the ions, as if herein were to be found the driving force of such reaction, the electromagnetic force-field theory attributes all reactions and reactivities to the opened-up systems of the molecules independently of whether ions are formed or not. The formation of ions according to this theory is a secondary phenomenon running concurrently with the primary cause of reaction.

The second method of opening up the closed fields is by the influence of light. Due as they are in the first place to the rotation of the electrons

of the constituent atoms, it follows that the force fields must be capable of absorbing those rays of light which have the same vibration frequency as that of the electrons. The light in being absorbed does work upon the closed fields and opens them, and this gives a rational explanation of the selective absorption of light. An example of the opening up of the closed molecular force field by means of light is found in the union of hydrogen and chlorine. When in the dark and at ordinary temperatures, the force fields of these gases are closed and they have no action upon one another. Under the influence of ultraviolet light the reaction to form HCl proceeds owing to the opening of the closed fields by the light, and the amount of combination is a function of the amount of the light energy that is absorbed.

In considering the work done by the light upon the molecules by which it is being absorbed, it was pointed out that the effect produced is to open up the closed fields of these molecules. When a substance is dissolved in a solvent it is clear that there must be set up generally an equilibrium condition. Some of the molecules will have their closed fields opened while others will not, and so an equilibrium is established, and upon this equilibrium the reactivity of the system depends. When such a system absorbs light the tendency will be for the light to increase the number of molecules having their fields open. The equilibrium previously existing is, therefore, shifted towards the reactive side, a new photodynamic equilibrium being established. The whole of the phenomena of photocatalysis can thus be explained on these lines.

The mechanism of the opening up of a closed force field may now be dealt with in greater detail. The general statement has been made that a given closed field may be opened by the influence of a solvent or by the influence of light, the action of the light being evidenced by the selective absorption of definite rays. If now the case be considered of a complex molecule, it is clear that the force field of that molecule will be complex. There must exist in such a complex field a network of potential gradients and the influence of the solvent in opening up the field will depend upon the nature of that solvent. It would be expected that the influence of a solvent upon a complex force field would be progressive, and that it would attack various portions of the field in turn. It indeed follows that the opening up of a complex field must take place in definite stages, the number of stages depending upon the complexity of the field. Each of these stages will be influenced by light so that each stage must be characterized by its power of absorbing definite light rays and may be differentiated in this way because the light waves absorbed by the various stages will be different. Each of these different stages mark steps in the opening up of a given force field and, therefore, are functions of a given molecule with a definite primary structure. The number of possible stages

will depend upon the complexity of the force field and these stages in turn may be called into play by the use of suitable solvents. Very typical examples of compounds which are opened up in stages are the β -substituted naphthalene compounds, which as a rule in alcoholic solution show three absorption bands. Three stages in the opening up of the force fields must, therefore, coexist in the solvent, each one characterized by its power of absorbing definite rays of light. In concentrated sulfuric acid solution the absorption spectrum is very different, since other stages are called into play, but usually one of these stages at least is common to the two solvents.

Certain experimental evidence may now be presented which gives very clear and decisive support to the theory. Since the opening-up process takes place in stages, and since each stage is characterized by its light absorptive power, it should be possible to follow the course of a chemical reaction and to trace the appearance of the stages by optical methods. Each opened-up stage must possess a definite reactive power towards other molecules. It is probable that a particular and definite stage must be reached before any specific reaction can occur. By this it is meant that if it be desired to induce a definite reaction towards a definite reagent it is necessary in all probability to open up the closed force field to one definite stage. Any earlier stage in the opening up will not endow the system with the required reactivity. In short, it may certainly be assumed that while each stage in the opening up possesses a definite reactivity, a certain limiting stage must be reached before any particular reaction can proceed.

Some years ago Miss Marsden and I investigated the absorption spectra of certain aromatic amino-aldehydes and ketones and we have found that the alcoholic solutions of these compounds exhibit a well-marked absorption band.¹ The addition of a small quantity of alcoholic HCl to any one of these solutions causes the development of a yellow or red color which disappears when more of the acid is added. This color is due to the appearance of a new absorption band nearer to the red than that shown by the parent compound. On the addition of the excess of acid the absorption spectrum changes to that of the hydrochloride of the amino base, which somewhat resembles that of the free base itself. It is clear from these results that the conversion of the amino bases to their hydrochlorides is not simply an addition reaction. There is no doubt that it is not the amino compound such as exists in alcoholic solution which forms the salt, but that the first quantity of acid converts the base into an intermediate form and *it is this intermediate form which reacts with more acid to give the salt*. These results at once extend our view of chemical reaction, in that they undoubtedly prove the existence of a hitherto unrecognized

¹ *J. Chem. Soc.*, 93, 2108 (1908).

intermediate stage; they also afford a definite proof of the force-field theory, for it was exactly this phenomenon which was shown above to be the direct result of the application of the theory to chemical reaction. The addition of the first quantity of HCl opens the closed fields to a higher stage, which is evidenced by its characteristic light absorptive power, and the field must be opened to this stage before the molecule can react to give the salt. These results also have a bearing on the application of the theory to catalysis. When the above amino compounds are treated with methyl iodide they tend to give their methyl derivatives. The velocity of this reaction is known to be materially increased when some acid is added. The acid has been shown to open up the closed systems to a higher stage with a greater reactivity, and, therefore, it acts as a positive catalyst in the methylation of these compounds.

Exactly analogous results have been obtained by Mr. Rice and myself in the sulfonation of aromatic phenol ethers.¹ In this case it was found possible to convert the whole of the reacting substance into the intermediate form and to observe its change into the sulfonic acid. In the former case we succeeded only in obtaining a small quantity of the amino base in the intermediate and more reactive form owing to the affinity between this form and the acid. In fact the maximum amount of this stage is obtained when only about 0.2 equivalent of HCl is added. In the sulfonation reaction, when the compounds are dissolved in cold concentrated sulfuric acid they are in many cases entirely converted into the intermediate stage, which frequently is characterized by its absorption of visible light so that the solution is visibly colored. On standing, the system is slowly changed to the sulfonic acid and the progress of the reaction can be followed with the spectroscope. The absorption spectrum of the sulfonic acid differs entirely from that of the intermediate stage, and somewhat resembles that of the original substance in alcoholic solution. It is, perhaps, worth mentioning that if the sulfuric acid solution, before the sulfonation has taken place, is poured onto ice the original compound is recovered in a pure state. These two investigations establish beyond any doubt the existence of the intermediate stage in a chemical reaction such as was deduced from the force-field theory.

The fact that the existence of the various stages in the opening up can be recognized by their characteristic light absorption enables us to interpret absorption observations with considerable certainty. These phenomena and their explanation will be fully dealt with in a subsequent paper, but reference may be made to one statement given above, namely, that nitrobenzene is an amphoteric substance. Mr Rice and I have found that the nitro derivatives of benzene tend to exist with their force fields

¹ *J. Chem. Soc.*, 101, 1475 (1912).

very definitely closed.¹ This results from the difference between the affinities of the phenyl nucleus and the nitro group. Such a compound would naturally tend to be affected differently by a strong acid and by a strong base. The absorption of nitrobenzene in solution in dimethylaniline and in concentrated sulfuric acid is entirely different; indeed, the former solution is colored red while the latter is colorless. Clearly, therefore, the manner of opening up the force fields is different; according to whether an acid or basic solvent is used and so we may speak of nitrobenzene as being amphoteric.

It was pointed out above that in the case of inorganic acids, bases, and salts, ionic dissociation is the extreme case in the opening up of their force fields. Now the effect of the selective absorption of light by a solution is to shift the equilibrium between the opened-up molecules and unopened-up molecules towards the reactive side, that is, to increase the former relatively to the latter. It should, therefore, be possible to increase the amount of ionization of a salt in solution by the action of light, and such effect should evidence itself in the catalysis of a given reaction or by an increase in the electrical conductivity of a solution. As a general rule, however, the force fields of inorganic salts are relatively simple and so the wave length of the light selectively absorbed by their solutions will be very short. Very few inorganic salts (except those visibly colored) exert selective light absorption in the region of the spectrum that can be photographed with a spectrograph in air, and therefore the absorption bands must lie beyond the frequency $1/\lambda = 5000$. There are, however, a few cases which can be experimented with and in one of these, namely, the chloroplatinic acids, Boll and Job² have found that under the influence of ultraviolet light the electrical conductivity of their solutions is materially increased. This is exactly what the force-field theory foretold.

An important confirmation would be found if it were possible to prove the catalysis of a simple inorganic reaction by the influence of light. As a general rule the velocity of such reactions is so great that the measurement of an increased velocity is precluded. There is one case, however, namely, that of KI and $\text{Hg}(\text{CN})_2$, which do not react in aqueous solution to give HgI_2 . The aqueous solution of each salt is diactinic to all the rays of light above $1/\lambda = 5000$ and, therefore, their absorption bands must lie at still shorter wave lengths. Such very short waves of light may be obtained from a hydrogen vacuum tube fitted with a fluorite window, and as such very short light waves are absorbed by air all experiments with them must be carried out *in vacuo*. A mixture of the two salts, finely powdered and slightly moist, was placed in a vessel cemented to the fluorite window. This vessel was exhausted so as to allow the rays to reach the

¹ *J. Chem. Soc.*, 103, 2085 (1913).

² *Compt. rend.*, 154, 881; 155, 826 (1912).

powder and it was then found that very small quantities of HgI_2 were superficially produced where the light fell on the mixture. These experiments must be looked upon as still being incomplete, but as far as they have gone the results are eminently satisfactory. It is in organic chemistry that the force-field theory finds its most obvious application, for so few of the reactions are ionic. For example, the opposite affinities of the nitro group and the phenyl nucleus give the key to the nitration of aromatic compounds. It is clear that when the latter are treated with HNO_3 , addition complexes tend to be formed in which the closed fields are opened up. Such addition compounds, if the potential gradients are sufficiently steep, will by transference of electrons give the nitro compound and water. It may readily be possible that the affinity of HNO_3 be not strong enough to open up the closed fields of the aromatic compound and in such a case it naturally will be advisable to use another strong acid as solvent. This explains why glacial acetic acid and concentrated sulfuric acid are so valuable in carrying out the nitration process. The power possessed by sulfuric acid in opening up the fields of aromatic compounds has already been mentioned and it is evident that its influence on the nitration reaction is not simply to be explained as that of a dehydrating agent. Again, the absence of action of HNO_3 upon the paraffins is also accounted for, since the spectroscope shows that there is no mutual influence between the two. Further, toluene is oxidized to benzoic acid by moderately concentrated HNO_3 , for its force field is not sufficiently opened to give the nitro derivative, but it is nitrated readily enough in a mixture of HNO_3 and H_2SO_4 . One further point of interest in the nitration of aromatic compounds is afforded by such compounds as *p*-dimethyltoluidine, which gives 1-methyl-3-nitro-4-dimethylaminobenzene when treated in HCl solution with NaNO_2 but gives 1-methyl-2-nitro-4-dimethylaminobenzene when dissolved in a mixture of HNO_3 and H_2SO_4 . The course of the reaction depends on the manner in which the force field of the amine is opened up.

There is some temptation to continue giving instances of phenomena which are simply explained by the force-field theory, as, for example, the unstable highly colored nitrophenol ethers of Hantzsch and Gorke¹ and similar compounds. One might point out that these compounds are simply an opened-up phase in metastable equilibrium. They are prepared from a salt in which the complex radical already exists in an opened-up condition. At the moment of formation the derivatives will also exist in a similarly opened-up condition and if due care be taken such derivatives may be preserved in that condition. In the presence of a suitable catalyst the metastable opened-up force field will condense until that condition is arrived at which is characteristic of the ordinary form of the com-

¹ *Ber.*, 39, 1073 (1906).

pound. This explanation of the existence of these unstable compounds, many of which have now been prepared, is very much simpler and more rational than that usually adopted, namely, that such bodies are chemical isomers of the stable modifications. The latter explanation generally involves the wandering of a radical, which experience derived from other compounds would not lead us to expect. Again, the present theory accounts at once for the abnormal reactivity of these unstable substances, because they have their force fields opened up to a high stage and they, therefore, obviously will be more reactive than the stable modifications.

The theory may also be applied to the phenomena of allotropy. It has already been shown by Smits that a most reasonable explanation of allotropy is to be found in the existence of definite molecular species, each allotropic modification being an equilibrium mixture of two or more such species.¹ The possibility of the existence of these molecular species is at once furnished by the force-field theory, for such species would simply be constituted by various complexes with their force fields in different states of condensation. The existence of such complexes is a very obvious deduction from the present theory, and, indeed, the theory would lead to the expectation of the phenomenon of allotropy being very wide spread. Our knowledge of allotropy, however, is rapidly being extended, for recent work² shows that the power of existing in allotropic modifications is possessed by numerous elements previously supposed to be confined within the limits of one form.

An interesting and somewhat suggestive conclusion is arrived at if the influence of an external magnetic field upon the molecular force fields is considered. The effect of such an external field on the force fields of the atoms of elements is shown clearly enough by the Zeeman effect. That there must result some effect when a molecular force field is brought into an external magnetic field is obvious. Since the former are electromagnetic in type it is clear that they will become keyed with the external field. The molecules will become polarized as it were, and unless the molecules are perfectly symmetrical as regards their force fields, a skew effect will tend to be established, since the external force lines are stationary. Such skew systems of force lines will result in the unequal retardation of light waves passing through the system, and, therefore, a plane-polarized beam of light will undergo rotation as regards its plane of polarization. It would, seem therefore, that the phenomenon of magnetic rotation also finds its explanation in the present theory. The suggestiveness of this is to be seen in the fact that it may be extended to the phenomenon of stereoisomerism and optical rotation generally. If the principle, advanced above, of the skew effect being the origin of the rotation of plane-polarized

¹ *Proc. K. Akad. Wet. Amsterdam*, 14, 788 (1912).

² E. Cohen, *Ibid.*, *passim*.

light be accepted, then the explanation of optical rotatory power follows naturally enough. The force field of any molecule which is asymmetric must of necessity itself be asymmetric, with the result that a skew effect will exist in the surrounding ether causing the rotation of the plane of polarized light. Now when the condensation of the force lines due to the several atoms of a completely asymmetric molecule is considered, there must be at least two ways in which such condensation can take place. In each case the same amount of energy will escape and the two skew effects resulting from such condensations will be equal and opposite. We, therefore, will have two entities almost identical if not entirely identical in chemical properties but with equal and opposite powers of rotating the plane of polarized light. The amount of rotation will depend upon the amount to which the force field has condensed. If such condensed force fields be attacked by solvents the rotatory power will tend to be altered. Again the rotatory power will be influenced by temperature, since it is obvious that the influx of energy, whether by increase of temperature or otherwise, will tend to open the fields and alter the skew effect. It equally follows that by the opening up of the condensed fields to a particular stage the skew effect can be nullified, with the result that racemization may ensue.

It is not necessary to emphasize the inherent advantage that this conception possesses over the old notion involved in the Le Bel and van't Hoff theory of the interchange of atoms or groups of atoms. After all, such interchange is abnormal and does not appear to take place in any other case with that readiness with which it is postulated to occur in stereochemistry. As a general conclusion drawn from the field of organic chemistry it may fairly be stated that the wandering of atoms or groups does not take place unless the product of such reaction is more stable than the original compound. The Le Bel and van't Hoff theory postulates the completely reversible interchange of groups in a completely asymmetric molecule. Such, indeed, might be accepted in a perfectly symmetrical system but where the asymmetry is an essential factor of the problem the process is antagonistic to the canons of organic chemistry.

The application of the force-field theory is based entirely on the principle of the rotatory power being due to the skew effect in molecular force fields. The dextro and laevo rotations are both the properties of one single primary structure, no isomerization being necessary to account for these phenomena. Although the present theory differs in one essential respect from the classical one, yet the whole is based on the complete asymmetry of the molecule, which is the real basis of the older theory.

The extension of the principle to all the phenomena of isomerism is sufficiently obvious to need no special discussion. Some emphasis must be laid on the fact that it is by no means necessary that there shall be one way and only one way in which the condensation of a given set of

force lines can take place, quite apart from the fact that individual stages in any one condensation process may have the power of metastable existence. The phenomena of geometric isomerism belong to the former category, while the highly colored unstable nitrophenol ethers of Hantzsch and Gorke and similar compounds belong to the latter.

If two differently condensed fields are obtained from one set of force lines, it is possible that the two condensed fields may be opened differently by solvents, and, therefore, the two substances will have different reactivities. Such differences usually are accounted for by attributing different primary structures to the compounds, but it would seem that this is entirely unnecessary.

Summary.

1. The existence of molecular force fields due to the electromagnetic fields of the constituent atoms is dealt with. It is shown that these force fields afford an explanation of chemical reactivity and reaction.

2. To the closed force fields and their opening up by the influence of solvents or light may be attributed all the phenomena of chemical reaction. Ionic dissociation is one special case of the whole.

3. In the existence of definite stages in the opening up of a given complex field, each with its power of absorbing definite light rays, is to be found the explanation of differently colored derivatives from the same compound.

4. The theory leads to the existence of intermediate stages in a chemical reaction and such stages have experimentally proved to exist.

5. When a compound is dissolved in a solvent an equilibrium is set up between the opened-up and non-opened-up molecules of the solute. Such a system has the power selectively of absorbing light rays, the effect of the light being to increase the number of opened-up molecules and thus to shift the equilibrium towards the reactive side. Some preliminary experiments on the photocatalysis of the reaction $\text{Hg}(\text{CN})_2 + 2\text{KI} = \text{HgI}_2 + 2\text{KCN}$ afford considerable support to this view.

6. The theory would also seem to afford a reasonable explanation of allotropy, magnetic rotation, stereoisomerism, optical rotatory power, and generally the phenomena of isomerism as a whole.

LIVERPOOL, ENGLAND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE AND THE WOLCOT'S GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE HEATS OF COMBUSTION OF AROMATIC HYDROCARBONS AND HEXAMETHYLENE.

By THEODORE W. RICHARDS AND FREDERICK BARRY.

Received January 30, 1915.

During the last ten years, extensive series of thermochemical investigations have been carried on in the Harvard laboratories with the help.

of the adiabatic calorimeter, which has been modified in various ways to meet the requirements of different sorts of problems.¹

One of the earliest of these investigations was concerned with the measurement of heats of combustion,² and yielded results proving the efficacy of the adiabatic principle. In a second research of similar character, the effective procedure already developed for the complete burning of organic liquids in the explosion bomb was further improved;³ and the method was shown to be capable of such a degree of precision as to permit a quantitative comparison of the heats of combustion of isomeric substances, magnitudes heretofore often indistinguishable. The present paper describes further measurements of such constants; the outcome shows a distinct gain in consistency and accuracy even over the immediately preceding Harvard work. The concordance of the values obtained in some of the series of measurements, as recorded in this paper, indicates a degree of precision comparable with the accuracy of much exact quantitative analysis—even in some accepted determinations of atomic weights. The investigation seems at least to have clearly shown that heats of combustion may now be determined, by a method at once simple and facile, with a precision limited only by the efficacy of processes of purification with respect to the material used and by the possible accuracy of thermometric measurements when mercury instruments are employed. The data here submitted indicate that these limitations do not stand in the way of very exact measurement.

An accumulation of data of this degree of trustworthiness should lead to comparisons of a very interesting and suggestive character. If the corresponding heats of vaporization, heat capacities, and heats of formation of the products of combustion can be determined as accurately, general inductions may perhaps be drawn from such data concerning the relationships between molecular configuration, and changes of free energy and internal energy. Among the many aspects of the general connection between chemical structure and physical property, none can be more interesting or important than this.

When so many data are necessary, ease and speed of experimentation are imperative. On this account, the simplicity of the method as here described is evidently one of its important advantages. The mercury

¹ For a résumé of the earlier part of this work, see Richards, *THIS JOURNAL*, **31**, 1275 (1909). The method was first proposed in a paper by Richards, Forbes and Henderson, *Proc. Am. Acad.*, **41**, 1 (1905); *Z. Physik. Chem.*, **52**, 551 (1905).

² Richards, Henderson and Frevert, *Proc. Am. Acad.*, **42**, 573 (1907); *Z. Physik. Chem.*, **59**, 532 (1907).

³ Richards and Jesse, *THIS JOURNAL*, **32**, 268 (1910). Other applications of the method are to be found in papers by Richards and Jackson, *Z. Physik. Chem.*, **70**, 414 (1909); Richards and Burgess, *THIS JOURNAL*, **32**, 431 (1910); Richards, Rowe and Burgess, *Ibid.*, **32**, 1176 (1910); Richards and Mathews, *Ibid.*, **33**, 863 (1911); Richards and Rowe, *Z. Physik. Chem.*, **84**, 585 (1913).

thermometer, which has been decried by some commentators, has the great merit of direct and convenient reading. Moreover, this instrument suffers from less suspicion of inaccuracy arising from thermal conduction than the electric instruments; and is of course wholly free from the very persistent and subtle errors due to stray electromotive forces. It is true, of course, that the mercury thermometer has its own errors, which must be carefully guarded against, but the most disturbing of these is the change of the zero point, which does not come into consideration in differential work of this thermochemical type. Moreover, all the work described in the present paper is relative, so that by using the thermometer over the same range and under the same conditions with the different substances to be compared, the thermometric errors may be almost entirely eliminated. Its simplicity enables a single experimenter without assistance to carry out the work of combustion with the adiabatic calorimeter, and the work may be done with a minimum loss of time from maladjustment and from accident.

One must bear in mind also the fact that a higher degree of accuracy than to within 0.001° is not warranted by the purity of most organic substances, and that the mercury thermometer in good hands can easily reach this degree of precision. Of course, where great *sensitiveness* is required, a modern electrical resistance thermometer or multiple thermoelement can easily outdistance the mercury-in-glass instrument; but, on the other hand, one must not confound sensitiveness and accuracy. An example of this danger is afforded by a recent publication by W. P. White,¹ in which the temperatures are given to within 0.0001° , although the accompanying diagram shows that readings made on different days deviated as much as 0.01° . The correspondence of the results with the empirical curve, moreover, was often even much worse than this, although this does not clearly appear in White's abbreviated statement.² This paper was the best authority on this subject at the time when the work to be described was performed. It is doubtless true that, since that time, this experimenter and others have obtained better results with the thermoelement than the unsatisfactory showing of this paper of 1910;³ and the platinum resistance-thermometer may be yet better; but taking all things into consideration, after extended and intimate experience with a thermoelectric thermometer kindly made for us by Dr. White, we decided that the time had not yet come (1911) for the application of either highly sensitive but precarious instrument to the problem in hand.

¹ *Phys. Rev.*, 31, 162 (1910).

² The discrepancy referred to will be found on calculating the values, especially those corresponding to 40.0000° and 82.0000° , as pointed out to us by Prof. A. W. Rowe.

³ W. P. White, *THIS JOURNAL*, 36, 2292 (1914).

The investigations here described had two distinct aspects; first, the actual measurement of the heats of combustion of certain homologous and isomeric hydrocarbons; secondly, a study and criticism of the method employed, for the purpose of estimating and of controlling or eliminating the possible sources of error inherent in it.

Preparation of Materials.

Particular attention was paid to the purity of the hydrocarbons to be studied. Both natural and artificial compounds of carbon are liable to serious contamination with impurities, either of a similar kind or of widely different character, such as bromides or chlorides, some of which may find their way into the substance during the course of its preparation. For the purpose in hand, of course, the radically dissimilar impurities are usually more prejudicial than the similar ones, and the worst of all impurities, weight for weight, is water, because it has no heat of combustion whatever. In order to eliminate as much as possible these dangers, especial precautions were taken. The details for each substance are discussed below.

Benzene.—This substance was made from a commercially pure sample derived from coal tar. It was shaken with successive portions of sulfuric acid until the acid remained quite colorless after three successive agitations. The last traces of acid were removed by means of a solution of sodium hydroxide, and this, in turn, by repeated washing with water. The benzene thus prepared, after thorough drying with calcium chloride and with sodium, showed no traces of thiophene or its homologs on applying the delicate indophenin test with isatin and sulfuric acid, although the same reagents gave with the original material a deep blue coloration. The complete chemical separation of thiophene is necessary in the first place because it cannot be separated either by distillation or crystallization.¹ The sodium used for the final drying of the benzene was washed free from petroleum (under which it had been kept) with scrupulous care, because the paraffins of petroleum have a widely different heat of combustion from aromatic compounds of like boiling point. The metal was dried and cut in the air, washed for a long time with purified benzene, again cut and dried and pressed into wire through a clean press previously washed with benzene, the first portions of the wire being rejected. The dried liquid was crystallized with the greatest care, especial pains being taken to prevent access of the moisture of the air. During the first three crystallizations a slight change in the freezing point was noted as the freezing progressed; but in the fourth and fifth, the substance

¹ The boiling points are: benzene, 80.2°; thiophene, 84°. Thiophene separates with benzene when this is crystallized, in a solid solution which is 42% as concentrated the original liquid solution. Bijlert, *Z. phys. Chem.*, 8, 343 (1891); Beckmann, *ibid.*, 22, 609 (1897).

gave a melting point constant to within 0.003° during the freezing of a large part of the liquid. This constancy in the freezing point indicates a presence of less than 0.01% of water.¹ The final value of the melting point of benzene was found to be 5.484° , a value very close indeed to that (5.483°) since found by Shipley and one of us in an investigation dealing especially with the subject.²

Toluene.—Pure toluene was prepared by fractionation of the commercial distillate. This material was first agitated with several portions of sulfuric acid, and otherwise treated by a procedure similar to that followed in the first purification of benzene. The product was free from olefenes and from thiophene and its homologs. It was dried with carefully prepared sodium which had been freed from paraffin oils by evaporation, and by long continued soaking in toluene.

This purified material, which contained besides benzene and xylene probably no other noticeable impurities, was fractionated from a still of special construction, a description of which has been published elsewhere.³ The product of 40 cc. which distilled within a range of less than 0.01° was called *toluene A*, and was dried at 100° over sodium and kept over sodium. Of the two other samples, prepared by redistillation of the other distillate, one called *toluene B*, distilled over about the same interval as *A*, and another, *toluene C*, which was much less pure, distilled over 0.1° . The boiling point of the purest sample was taken with great care and found, by means of calibrated Beckmann thermometer, to be 10.25° above the boiling point of water under the pressure of 752.6 mm. Since under this pressure the boiling point of water is 99.726° ,⁴ that of toluene is 109.98° . According to the data of Young,⁵ this would become 110.31° at 760 mm. pressure.

Ethyl Benzene.—Two samples of ethyl benzene were prepared. One was made by the Fittig reaction from bromobenzene and ethyl bromide with sodium. These materials were themselves very pure to begin with, the bromobenzene having been made from thrice recrystallized thiophene-free benzene, and the ethyl bromide having been carefully purified by

¹ W. Hertz, *Ber.*, 31, 2669 (1898); miscibility of benzene with water; also Paterno, *Gazz. chim. ital.*, 19, 460 (1889), on lowering of the melting point.

² THIS JOURNAL, 36, 1825 (1914).

³ Richards and Barry, THIS JOURNAL, 36, 1787 (1914).

⁴ Weibe, *Z. Instr.*, 13, 329 (1893) from the data of Regnault; Landolt und Bornstein, "Tabellen," 1912 Aufl. p. 365.

⁵ Data in Crafts, *Ber.*, 20, 709 (1887), and Young, *J. Chem. Soc.*, 81, 777 (1902). Summarized in Young, "Fractional Distillation" (1903), pp. 14, 15. The boiling point here given is in accordance with the value submitted by Neubeck, *Z. physik. Chem.*, 1, 656 (1887), and by Kahlbaum, *Ibid.*, 26, 603 (1898), which are respectively 110.3° and 110.4° . It does not agree with those given by Young, *J. Chem. Soc.*, 73, 906 (1898) and by Timmermans, *Bull. Soc. Belg.*, 24, 244 (1910), which are, respectively, 110.8° and 110.7° .

fractionation. Thus it was possible to prepare a sample of ethyl benzene which when fractionated showed only traces of the acrid compounds which usually contaminate this hydrocarbon, possessing an agreeable, ethereal odor, and being perfectly colorless. At first it distilled wholly within a degree, and upon fractionation, after complete drying, it yielded a product which redistilled within three-tenths of a degree. This substance was labelled *ethyl benzene B*; and that part of it which distilled within one-tenth of a degree, *ethyl benzene A*. The boiling point of *ethyl benzene A* was determined during the final redistillation, which was carried out in a still of the same general design as that used for the fractionation of toluene, but of smaller dimensions. A small Reichsanstalt standardized Anschütz thermometer hung suspended in the tube, visible through the mica-covered apertures which pierced the asbestos insulation of this tube at the desired points. The boiling point was 136.03° (mean temperature) at 761.1 mm. which becomes 135.98° at 760 mm. pressure.¹

That all this trouble was worth while was shown by the combustion of a cruder sample made from the rejected residues in the fractionation of *ethyl benzene A*. It boiled over four degrees and yielded a result for the heat of combustion 0.4% lower than that of the pure product.

Another sample of pure ethyl benzene, labelled *ethyl benzene C*, was made by the condensation of benzene with ethyl bromide under the influence of aluminum chloride in the presence of finely divided mercury.² The substance was prepared with the same care as that observed in making the other material, and the product was equally well fractionated. Moreover, it distilled at almost the same temperature. It yielded, nevertheless, lower values for the heat of combustion, as will be seen; but there is every reason to believe that the discrepancy was due to the presence of a trace of bromine, because an appreciable quantity of bromide was found in the bomb after the combustion. It is uncertain whether all of the bromine could be recovered in the bomb, and also in what way this substance was originally combined, hence the exact correction for the presence of this bromine is impossible; but an approximate correction is made below, which shows that the amount of the impurity was of the same order as the difference between the two series of results.

Mesitylene.—The specimen of this substance, prepared as usual from acetone, was carefully fractionated. Fifty per cent. of the raw material distilled within 0.3° . After five distillations half of the ma-

¹ Cf. R. Schiff, *Ann.*, 220, 92 (1883), who gives the boiling point of ethyl benzene as 135.7° at 758.5 mm. This value reduces to the mean 135.8° at 760 mm. Perkin, *J. Chem. Soc.*, 69, 1191 *et seq.* (1896) gives the boiling point as 135.5° .

² Radziewanowski, *Ber.*, 28, 1138 (1895).

terial had been brought within the range 0.2° . The corrected boiling point of the portion taken at the peak of the accumulation in the distillate was 164.72° at 760 mm., including all corrections.¹ Three samples were burned: (A) having a boiling point between 164.6° and 164.7° , (B) having a boiling point 0.1 of a degree higher; and (C) 0.2 of a degree lower. In spite of these different boiling points, it will be seen that all of the material gave essentially the same quantitative results. The thermometer had been standardized by the Reichsanstalt.

Pseudocumene.—A specimen of this substance (1,2,4-trimethyl benzene) made by rectification of the commercial distillate furnished by a competent German firm, showed a fairly constant boiling point near 169° . After drying over sodium on the steam bath, it was fractionated by eight distillations, a fraction being finally obtained which redistilled within a range of 0.1° , as in the case of mesitylene. The boiling point of this material averaged 169.27° corrected to 760 mm. This specimen was labelled *pseudocumene A*. Here again we thought it worth while to test the heat of combustion of a distillate with a lower boiling point in order to determine as before if the inevitable impurities might have a perceptible effect upon the heat of combustion. No important difference was, as a matter of fact, observed. The boiling point of the pseudocumene, as we have found it, lies between the values given by Warren and Perkin, which are, respectively, 169.8° and 168.2° .²

Normal Propyl Benzene.—This substance and all the following substances were prepared from benzene or of substances made from benzene which had been carefully purified in the manner already described. They were in every case carefully fractionated and dried by distillation from sodium, just before being used for combustion, and were usually kept sealed in glass tubes or preserved in tightly clamped glass-stoppered bottles. As all but one of the hydrocarbons were made either by the Fittig or Friedel-Crafts synthesis, exceptional precautions were taken that the final products might be freed from halogen, because the halogen derivatives have much lower heats of combustion than the hydrocarbons. That this purpose was accomplished was shown by tests according to the Carius or the Pringsheim method.³ Moreover, the residues in the bomb after combustion were tested with silver nitrate and nitric acid. In no case was more than a very slight opalescence observed, corresponding to an amount too small to have any perceptible effect upon the heat of combustion. The absence of these halides leads one to hope that the corresponding alcohols from which they were made were also absent. Alcohols are

¹ Schiff, *Lieb. Ann.*, **220**, 94 (1883) gives 164.5° and Perkin, *Loc. cit.*, 164.1° .

² Warren, *Z. Chem.*, **1865**, 666; Perkin, *Loc. cit.*

³ Pringsheim, *Ber.*, **36**, 4244 (1903); *Ibid.*, **37**, 2155 (1904).

especially troublesome, because they form mixtures having constant boiling point with alkyl halides and with the hydrocarbons.¹

Normal propyl benzene was synthesized from bromobenzene and normal propyl bromide with sodium. The reaction was retarded by cooling with ice in order to minimize molecular transposition. The product, having been once distilled, was treated with washed and dried ether and magnesium turnings to which a small quantity of activated magnesium had been added, together with a crystal of iodine, to catalyze the reaction. This mixture was refluxed for three hours, then treated with water and separated. The bromobenzene boiled at 156.2° . Afterwards the product was boiled with alcoholic potash, washed with water, dried and fractionated. The final product boiled with great constancy within 0.1° , at 158.0° under 760 mm. pressure. Schiff² gives the boiling point as 158.5° at 751.6 mm.

Every test showed this hydrocarbon to be entirely free from halogen. It might have contained a small quantity of isopropyl benzene, but its odor and the constancy of its boiling point militates against this possibility. Even if much isopropyl benzene had been present, no measurable change would have been caused in the heat of combustion.

Other methods of making propyl benzene, such as condensation of benzyl chloride with ethyl bromide and of iodobenzene with normal propyl iodide, were attempted, but were not as successful.

Isopropyl Benzene.—Two samples of isopropyl benzene were prepared, one by the condensation of isopropyl iodide and benzene by the Freidel-Crafts reaction; the other from isopropenyl benzene, made by the Grignard reaction from acetophenone after the method described by Klage.³

The Freidel-Crafts material was prepared in the simplest possible way, by the use of anhydrous aluminum chloride alone. The use of mercuric chloride and metallic aluminum as catalyzer was abandoned; because of the suspicion that mercury alkyl compounds might thus be formed. The reaction ran slowly for two days in a closed flask, then rapidly when refluxed for three hours; it was stopped by a bath of ice water, and hydrochloric acid was added to separate the emulsion.

The product was freed from hydriodic acid and iodine and from hydrochloric acid by repeated washings in sodium hydroxide solution, was carefully dried and then distilled. The distillate was boiled with alcoholic potash for fifteen minutes, dried again and fractionated in the still used for the fractionation of ethyl benzene. The finally chosen fraction

¹ Ryland, *Am. Chem. J.*, **22**, 384 (1899); Young and Fortey, *J. Chem. Soc.*, **83**, 45 (1903). For a summary of these results, see Young, "Fractional Distillation" (1903), pp. 67, *et seq.*

² *Ann.*, **220**, 93 (1883).

³ A. Klage, *Ber.*, **35**, 2640 (1902).

boiled at $152.85\text{--}153.15^\circ$ under 765 mm. pressure,¹ and redistilled almost wholly within the same range. The product, which probably contained no isomeric hydrocarbon, yielded, after complete combustion under 20 atmospheres of oxygen, a residue which showed only a negligible opalescence when tested with silver nitrate and nitric acid. It was, therefore, a very pure product. This material was labeled *isopropyl benzene A*.

A second sample of isopropyl benzene was made by a radically different method with equal care. Acetophenone was added very slowly to the Grignard reagent at the temperature of melting ice; the ether was distilled off, and the residue then refluxed for six hours on the steam bath. The product, isopropenyl benzene, was then reduced by three times the reaction-quantity of sodium in absolute alcohol; and after the reaction, the product was washed and separated with dry ether, dried with anhydrous sulfate and twice distilled. The resulting liquid, of somewhat rancid odor, boiled at $152\text{--}153^\circ$. It was treated with alkaline permanganate until it showed no color-change after long standing, and until a sample added to a dilute solution of bromine and chloroform showed no evidence of further oxidation. This purified material was then fractionated in the usual way, and yielded a final fraction of 3 cc., which boiled at $152.5\text{--}152.8^\circ$ under 751.4 mm. pressure. It was distilled from sodium and yielded a final distillate of about 2 cc. This product was called *isopropyl benzene B*. It is to be noted that the boiling points of these two products were fairly close together, although not identical.

Tertiary Butyl Benzene.—This hydrocarbon was synthesized from pure benzene and a residual sample of isobutyl bromide by the Freidel-Crafts reaction. The isobutyl benzene formed is under these circumstances wholly converted to the tertiary by molecular transformation.² The hydrocarbon thus made having once been distilled and thoroughly dried, was fractionated, and a final distillate was at length obtained which came over wholly within 0.2° . Its boiling point at 751.4 mm. pressure was $168.8\text{--}169.0^\circ$.³ The yield of this pure substance from 410 g. of benzene, and 100 g. of isobutyl bromide was about 10 g. Upon combustion, the resulting water gave no opalescence whatever with silver nitrate.

Cyclohexane was prepared in a pure state from very pure benzene by the Sabatier-Senderens reduction.⁴ The benzene was vaporized at 65°

¹ Cf. Perkin (*Loc. cit.*) who gives the b. p. 152.9° . The b. p. given above reduces to the mean 152.3° at 760 mm.

² Schramm, *Monatshefte*, 9, 615 (1888); Gossin, *Bull. soc. Chim de Paris*, 41, 446 (1884).

³ Cf. Schramm (*Loc. cit.*) who gives the b. p. of this substance at 736 mm. as $167\text{--}167.5^\circ$. Data are not available with which to convert these boiling points accurately to 760 mm., and thus to compare them.

⁴ *Compt. rend.*, 133, 321 (1901).

in a current of pure hydrogen, which had been made free from all usual contamination, and carefully dried by passage over red hot copper gauze and solid potassium hydroxide. The mixed vapor was led at 160° through a coiled tube three meters in length packed with iron-free pumice, on which finely divided nickel had been deposited. This had been prepared in such manner that it was free from chlorides and other negative catalysts. The composition of the condensed vapor was tested by freezing-point determinations made after each attempted reduction. Only after the mixture has been passed eight times through the reducing coil was the reduction thus shown to be complete.

The approximate freezing points of these mixtures are of interest: the first condensate began to freeze at $+4^{\circ}$, the second at -4° , the third at -21° , the fourth and fifth below -22° , the sixth at $+2^{\circ}$, and the seventh and eighth at about $+6.3^{\circ}$. Thus the first was almost pure benzene, and as more and more of the substance was converted into cyclohexane the freezing point passed through the eutectic point (below -22°) and finally rose as the benzene was eliminated.

From 800 cc. of benzene, about 120 of cyclohexane were thus made. A greater yield could have been obtained by the use at all times of a condenser packed in a freezing mixture, for there was much loss through evaporation. The material thus made was twice crystallized, while mechanically stirred, in a Beckmann freezing-point apparatus similar to that used for the crystallization of benzene. The bath was kept very constant at a temperature slightly above the freezing point of benzene; and care was taken that the cyclohexane was not contaminated with water. About a quarter or a third was rejected at each freezing, hence about 60 g. remained of the pure material. The product of the first crystallization was labeled *Cyclohexane B*; that of the second, *Cyclohexane A*. After having been carefully dried, cyclohexane A was distilled in a side-tube still which held a standardized thermometer wholly enclosed, and showed a boiling point of 80.8° under 760 mm. pressure, which remained constant within visible limits (*i. e.*, at least to within 0.03°). The melting point of this material was found with great care by comparison with that of pure benzene, the procedure being precisely similar to that by which the melting point of benzene had been determined. It was found to be 0.485° above that of benzene, or 5.97° .

In spite of our care, it is not impossible that a trace of benzene remained in this substance. Accordingly, its heat of combustion may be slightly lower than the true value, but we believe that more care to avoid this difficulty was taken in the present case than in previous investigations of others.

Cyclohexane burns with such violence in the bomb as to cause trouble in the thermal measurement. In one case, which of course had to be re-

jected, the insulated electrode was blown out of the bomb. The two determinations which are later given, however, are probably not more than 0.1% in error.

Sucrose.—Pure sugar was made from the commercial granulated material by successive crystallizations. It was dissolved in 50% redistilled aqueous ethyl alcohol and crystallized by the addition of more alcohol and by cooling. The precipitate was thoroughly centrifuged, and the process of precipitation was repeated four times. It was dried under reduced pressure, repulverized in agate, and dried again. It was kept over fused potassium hydroxide in a desiccator, and was so dry that it acted like a powdered silicate, and did not adhere either to pestle or platinum vessel. This purest sample was labeled *Sugar A*. A similar less pure sample was prepared in the same way, with only three instead of four crystallizations, but its heat of combustion was identical within the limits of experimental error; hence its purification was really sufficient—the further treatment received by sample *A* had been an act of supererogation. In the course of the crystallization of this sugar, all the precautions which would be observed in a most accurate investigation upon atomic weights were taken. These are well known and recognized, and it is perhaps unnecessary to detail them here. It is enough to say that, both as regards purity of the liquids, care in filtration and all the other minutiae of the work, every effort was used to prevent the ingress of impurity.

The Bomb and the Details of Combustion.

The apparatus employed has been in part described in the publications already cited, but certain additional features require explanation. The bomb used was of the Atwater type,¹ wholly lined with platinum. Because leaden gaskets around the rim are easily corroded, and because electroplating of the lead with gold or covering it with strips of gold foil had proved troublesome and unsatisfactory, we used a gasket of pure, soft annealed gold. In the later determinations the whole top of the bomb, in addition, was lined with a circular sheet of pure, soft gold, which covered the gasket as well as the center.

The bomb itself had been altered in two respects. After use during several years the lining had become worn at the edge which bore upon the gasket. This edge was planed down, and a ring of triangular cross sections was cut out of it in such a manner that a double edge was presented to the gasket (Fig. 1). The alteration insured a more complete closing of the bomb by moderate pressure, and prevented leakage. To the bottom of the bomb, legs of heavy wire were attached, a centimeter in length; and thus an easy circulation of the calorimeter water beneath

¹ This instrument, together with its accessories, is described in detail by Atwater and Snell, *THIS JOURNAL*, 25, 659 (1903).

the bomb was secured. The instrument thus altered was found to be satisfactory in every way.¹

The calorimetric vessel was a cylindrical can of pure spun silver, brightly polished on the outside. This vessel was somewhat smaller than those

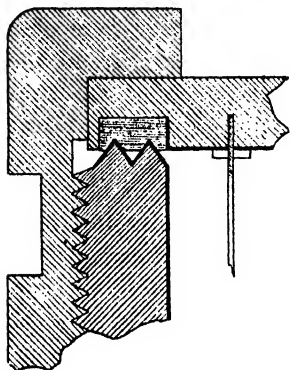


Fig. 1.—Section of edge of bomb (actual size). Showing double ridge pressed against gold washer.

previously used in similar researches; thus the heat capacity of the calorimetric system was reduced, with the result that the temperature-rise per gram of material burned was nearly half again as great as in former measurements.²

The calorimetric stirrer was of the usual vertical reciprocating type, consisting of two perforated rings firmly attached to slender vertical supporting rods; and provided with thin guiding wires which prevented engagement with the collar of the bomb. The supporting wires were cut to such a length that they never left the

calorimetric system and were insulated from the outer attachments by thin rods of vulcanite. As a result of this modification no heat was lost to the system by conduction, while the sucking in of outside air remained minimal.

The calorimeter was surrounded everywhere by a narrow air-jacket, being held by small pieces of cork within a slightly larger vessel of brightly polished nickel-plated copper, the walls of which were about the same thickness and conductivity as its own. The insulation was carefully tested electrically before and after each determination. This copper vessel, nicknamed a "submarine," was provided with a water-tight cover, pierced with tubes for the necessary entering parts of the apparatus. The cover, made of cast brass, was heavier than those formerly employed, and was supported by a correspondingly heavy rim of brass soldered to the jacket, which carried five swivelled thumb-nuts symmetrically arranged and permanently attached. Both cover and rim were perfectly plane on the bearing surface, so that the joint, protected by a gasket of

¹ A number of trial combustions were made with a Kröcker bomb of German manufacture. It was easily handled, and would in all probability have been a satisfactory instrument had it been constructed in accordance with the published and advertised design. As actually made, however, the lead gasket intruded into the bomb-chamber to such an extent that it was very badly corroded; moreover, the rim of the exposed part of the cover was of unprotected bronze; and the construction of the electric connection was flimsy and mechanically bad.

² By this alteration also, the surface of evaporation was reduced. Even in former work, however, in which larger vessels were used, error from heat absorbed by evaporation of the calorimeter water had been calculated to be negligible. See Richards and Jesse (*Loc. cit.*).

soft rubber, was easily made tight by gentle pressure and never leaked in consequence of the distortion of cover or rim, during several months of continuous use. In a practical way, this modification was important for obvious reasons. The somewhat lower conductivity of the cover (due to its greater thickness), was a matter of no moment, since the surface is small, and even with the greater thickness, the conduction of heat is very rapid. The whole calorimetric system, together with its protecting jacket, was held underneath a bath of dilute caustic alkali, the temperature of which could be regulated by the addition of sulfuric acid from a buret graduated as usual in tenths of a degree. The powerful stirrer and other mechanism of this external apparatus has been so often described that no further explanation is needed. The bath thermometer, placed on the opposite side of the bath from the acid-intake, was like the calorimetric instrument, and gave strictly comparable readings. Insulated ignition wires were led from the bomb electrodes through the chimneys in the cover of the calorimeter jacket which accommodated the stirrer. These chimneys were stopped above by cotton wool, loosely wired in place, in order to prevent circulation of atmospheric air. The stirring machinery was rigidly mounted, in such a manner as to insure fairly constant speed—a matter of first importance, as experience showed. The appended diagram shows the entire apparatus, drawn approximately to the scale (Fig. 2).

The calorimetric thermometer (maker's No. 11258) was one which had been made especially for this and similar work. It had been filled under an atmosphere of pure hydrogen, and the movement of the thread was prompt and regular. The scale, which was divided in hundredths of a degree, covered the temperature interval from 15.3 to 20.5°; the length of the 1/100° interval was about 0.8 mm., and intervals of 0.0005° could be readily estimated with a lens. Before reading, the thermometer was softly and evenly tapped upon the side; violent tapping, especially upon the top, may cause the column to jump and remain fixed several thousandths of a degree above its true point. This simple precaution is a very important matter. The best procedure for this particular instrument having been found, it was always practiced. The temperatures were always read to within 0.0005°, and the corrections were calculated also including the fourth decimal place, but this outcome was rounded off to the nearest unit in the third decimal place in the final recording of the results. The thermometer was read always with a very slowly rising temperature, never when the thread was falling.

This instrument has been four times standardized: by the Reichsanstalt in 1909 (P. T. R. No. 37900); by the United States Bureau of Standards in 1909 (B. S. No. 5506); and at a very great number of points by the authors in collaboration with Dr. A. W. Rowe in comparison with the

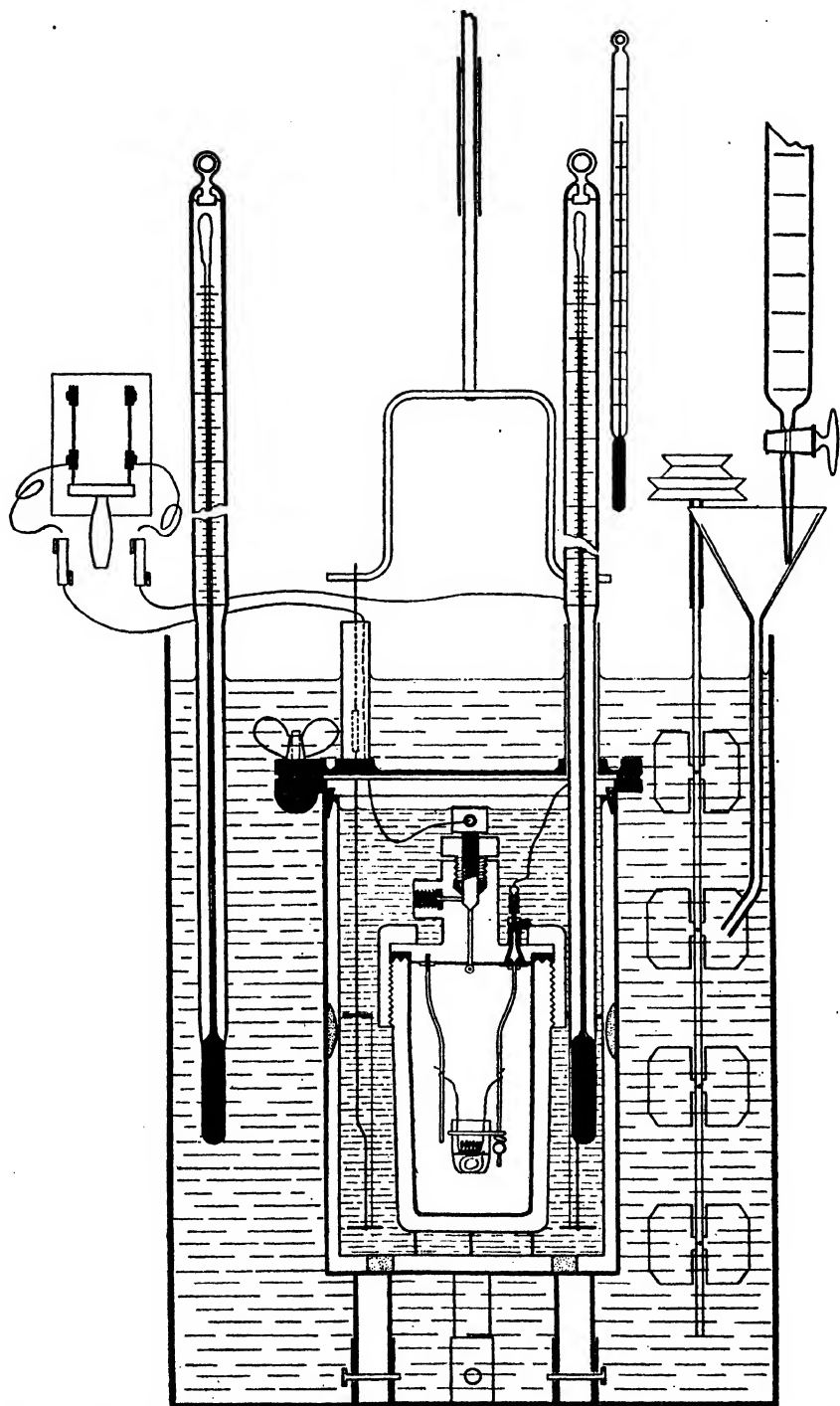


Fig. 2.—Complete assembled apparatus for calorimetric combustion. (In section.)

Baudin instruments 15200 and 15276 of the Bureau International des Poids et Mesures, and finally with the help of Dr. T. Thorvaldson. The Reichsanstalt work had been very crudely done, perhaps through a misunderstanding; on the other hand, the results of the Bureau of Standards at Washington corresponded fairly well with our own comparison with the Parisian Standard. The results are expressed in terms of the Parisian Standard as given by the Baudin instruments, but, as a matter of fact, it does not greatly matter which of these standards were used, as the work was wholly relative, and almost the same range was used for each experiment. If in the future it is found during the course of a critical study of the thermometric scale¹ now in progress here, that small corrections are in some cases necessary, these may easily be applied at any time. After some delay we have thought it best not to withhold the publication of this paper longer on this account.

It is worthy of note that such uncertainty as exists is not due to the mercury-in-glass thermometer used by us, but rather to the *standard to which it is referred*. This same uncertainty would apply to any other means (such as the electrical ones) of employing this same standard.

It should be noted that the instrument used in this work was always kept at temperatures near that of the room—it was never cooled to zero. Thus it was spared the internal upheavals which are caused in glass by any considerable changes of temperature.²

The hydrocarbon to be burned was dried with scrupulous care, and was sealed into small glass bulbs, previously weighed, in such manner that at room temperatures the bulb was completely filled. To make this possible the bulbs were made very thin, and were flattened on opposite sides; so that under high pressure they yielded until the liquid itself bore the strain, and at the higher temperatures they expanded readily under the internal tension (Fig. 3). The bulbs were filled by alternate heating and cooling, caused by contact with and removal from a piece of heated metal. A general heating of the bulb was dangerous, since under these circumstances the liquid evaporated almost explosively and often burst its fragile container. After filling, each bulb was kept at 16.7° in a water bath until constant in temperature; the liquid in the capillary was boiled out quickly by a small flame to a point close to the bulb; this was then chilled in cold water and sealed by a hot flame at the point from which the liquid had been thus withdrawn.³ The bulbs were cleaned carefully and were

¹ See THIS JOURNAL, 37, 81 (1915).

² These and other precautions are discussed in a recent paper by one of us, *Orig. Comm. 8th Intern. Cong. Appl. Chem.*, 1, 416 (1912).

³ The bulbs without their attached capillaries weighed from 0.3 to 0.5 g. They were designed to hold somewhat less than a gram of material; in every case such a quantity as would cause a rise in temperature of 3° when burned in this calorimetric system. According to the value of the heat of combustion of the material being used,

dried in a desiccator under reduced pressure. This process tested their ability to remain unbroken when placed in the partially exhausted tube. They were weighed to within 0.05 mg. with carefully standardized weights;

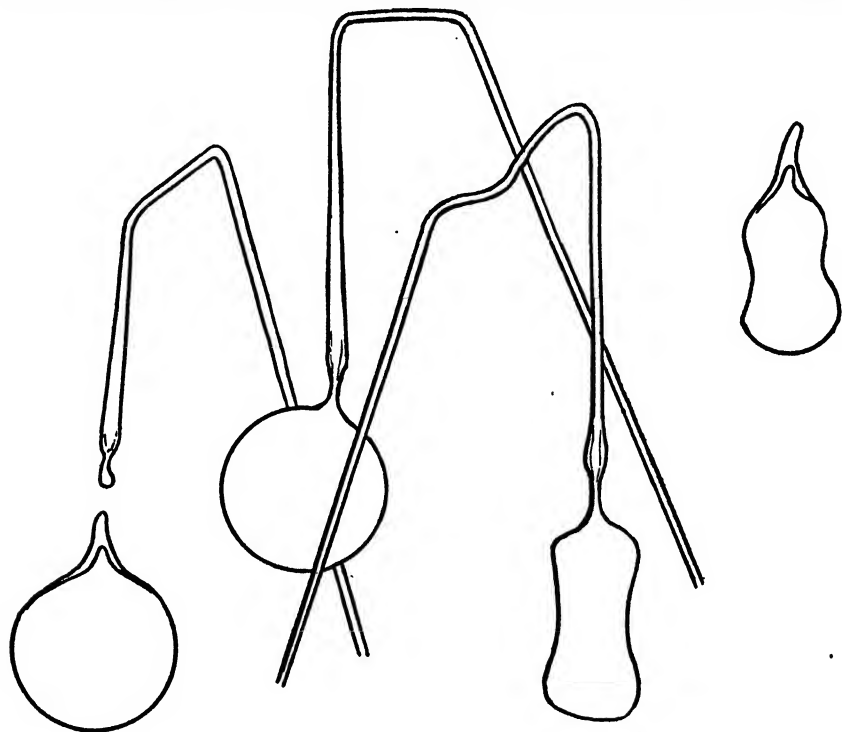


Fig. 3.—Glass bulbs for containing volatile liquids in various stages of preparation. (Somewhat larger than actual size.)

the weight was checked after a sufficient interval and was reduced to the vacuum standard. Leakage could always be detected by odor and by inconstancy in weight; of course all leaky bulbs were rejected.

The bomb was prepared substantially as in the latest of the previous investigations. A small, narrow, platinum crucible replaced the usual capsule; the bulb, placed at the bottom of this, was covered by a thin circular plate or shelf of glass (a microscope slide-cover), from which a small piece had been snipped to allow the easy escape of vapor.¹ Pure the bulbs were selected for size, which is, of course, easily measured by immersion. While the liquid was being boiled out of the capillaries, and during sealing, the bulbs were kept at the desired temperature in a thimble beaker, filled with water. The capillary protruded through a thick mica cover. Care had to be taken against forming tarry matter in the capillary by partial combustion, and against leaving residual liquid in the detached capillary. Loss of glass by volatilization in the blow pipe flame was negligible.

¹ Richards, Henderson and Frevert, Richards and Jesse, *Loc. cit.*

sugar in small quantity, usually less than 0.1 g., was spread evenly upon the little glass shelf; it was weighed by difference, and the weight reduced to the vacuum standard. The ignition wire of pure iron was cut to constant length (a procedure found to be as accurate as weighing), was coiled, and adjusted in such a way that several turns of the helix just touched the sugar. This precise adjustment was found necessary to prevent incomplete combustion and the formation of charred particles by spattering.¹ In consequence of the arrangement of the materials to be burned, the heat from the ignited sugar burst the bulb below it, and the vapors from the bulb had to pass through a zone of flame before they escaped into the combustion chamber. This favored completeness of combustion. Only occasionally when the bulb broke under pressure before ignition was the odor of unburned hydrocarbon detected in the open bomb.² Such trials were rejected.

Before the bomb was closed, 1 cc. of water was always introduced. This was in amount more than sufficient to insure the saturation of the enclosed air with water vapor before combustion, and thus to cause the complete condensation of the water formed by the reaction.

In order to diminish the amount of nitric acid formed during the combustion, the bomb, having been closed, was exhausted by air to a pressure of about 20 mm. of mercury. To the same end, as well as in order to reduce another correction, the ignition wire was made as short as seemed practicable; for the formation of nitric acid, *ceteris paribus*, seemed to result more from the combustion of the iron than from the burning of the hydrocarbon.³

The best oxygen pressure was found in these measurements to be in the neighborhood of 20 atm. Under a greater pressure the bulbs were likely to burst; moreover, at 30 atm., odoriferous gaseous products were formed. In all combustions the fairly constant pressure of 20 to 23 atm. was maintained, the variation in which could not have altered sensibly the heat capacity of the system.⁴

The colorimeter water, at a determined initial temperature somewhat

¹ This procedure, the general method, involving which was applied in previous investigations, has been here described in some detail, since of all involved it required the greatest nicety in manipulation; and determined in greatest measure the success of each operation.

² By the dilution of a known quantity of benzene vapor with successive additions of air, it was demonstrated that the odor test for unburned hydrocarbon was more than sufficiently sensitive to serve for the detection of all but quite negligible quantities. The benzene was chosen for this test because of its relatively faint odor.

³ This was shown by the parallel variation which was always observed between the corrections applied for wire burned and for nitric acid formed.

⁴ The oxygen used was made from liquid air. It had been analyzed for oxygen, and was found to contain never more than 2.5% of inert gas, largely argon. Subsequent tests showed it to be free from halogen.

below 16.5° , and always the same in amount was weighed to within ± 0.2 g.—an accuracy more than adequate.

The apparatus having been assembled and tested for insulation and correct adjustment, the whole calorimetric system was brought to thermal equilibrium in the neighborhood of 16.5° . The approximate temperature range expected had been estimated by calculation from the weights of the materials used; while the initial temperature had been selected in accordance with this value, usually so as to cause the final temperature to be near 20° . Effort was made to have both temperatures come upon smooth stretches of the curve of thermometer-calibration. The thermometer was cooled a trifle below the chosen point before immersion, so that initial readings could be taken on a rising thread. Equilibrium having been once established, observations were made at short intervals for 15 or 20 minutes, while the system was kept as closely as possible adiabatic. The rate of temperature rise due to stirring at the initial temperature was thus determined. Simultaneously, readings of the stem temperature and of the actual rate of stirring were recorded. This done, the charge was ignited and the temperature rise within was paralleled in the bath outside by the addition to the bath of sulfuric acid from the buret. It was found to be in no way difficult to hold the thermometer registrations of the bath temperature within 0.1° of those indicated by the calorimeter thermometer during the minute or more occupied by the rapid change of temperature; while toward the end, this correspondence could be maintained within 0.010 to 0.02° . Calculation, based upon blank experiments in which the rate of heat interchange was measured while differences of several tenths of a degree were maintained between the calorimeter and bath, indicated a much wider margin of safety in manipulation. The effective distribution of acid in the outer alkaline bath is an essential precaution. The rotary bath-stirrer completed 320 r. p. m., and was found to distribute the acid evenly in less than four seconds. The thermometric lag, occurring to the same extent with both instruments, is eliminated from consideration.

At the final temperature, which was approximately that of the environment, further readings were taken at intervals of two minutes until the rate of temperature rise became uniform; and thereafter at longer intervals for ten minutes or more. Thus the temperature rise due to stirring at the final temperature was determined. During this time also, the stem temperature and the rate of stirring were again recorded. The initial temperature had been read immediately before ignition. The final temperature was taken at any convenient time after the rise had become uniform. The time interval that had elapsed between these readings, usually about ten minutes, was known from the data; and the stirring correction was calculated for this interval from the observed rate at the

final temperature, at which it was unaffected by the sucking in of air from the outside, since this was at about the same temperature. The two observed rates of evolution of heat from stirring were usually closely the same; normally, that taken at the lower temperature was slightly larger, perhaps because of the greater viscosity of the water, but in such degree that no important error could have resulted in basing the correction upon the other. A correction derived from either the initial or the average rate would have approximated the true value somewhat less closely than that from the final rate, since the temperature rise was much more rapid at the start. This method of reading initial and final temperatures on almost stationary but very slowly rising thread, which is moving at nearly the same rate at both times, quite eliminates thermometric lag as a factor of inaccuracy in the difference between the readings.

The correction for stirring was somewhat variable, depending upon the speed, and the size and shape of the annular space between the bomb and the calorimeter wall. By placing thermometers at different heights, it was found that no stirring rate less than 65 strokes a minute was effective in preventing a dangerously persistent thermal stratification within the calorimeter; in consequence, the usual rate employed was 70 strokes a minute. The rise of temperature due to stirring at this rate might have been reduced by using a larger calorimeter, as in former work, but the advantage thus gained would have been slight in comparison with that lost. Because of its variability, the stirring correction was determined in each case to within a small limit of error.

The correction for stem exposure was in these determinations very small, since at the initial temperature there was but slight exposure and since the final temperature was near to that of the environment. Its magnitude was invariably less than 0.001° .

The correction for heat developed from that portion of the iron ignition wire actually burned was calculated from the known heat of combustion to Fe_3O_4 ; the small pieces of unburned wire found attached to the electrodes after the bomb had opened were always measured and allowed for.¹ The calculated value of this correction was checked by determinations carried out according to the usual procedure, in which wire alone was burned, of a length double that used in the combustions. These measurements verified each other and the calculated correction within the limit of observation. They proved, incidentally, that the electrical heating of this wire to ignite it, which had been made as uniformly slight as possible and calculated to be negligible, was so in fact.

The quantity of nitric acid formed in each combustion was determined by titrating the washings from the bomb with standard alkali. From this correction for heat developed in its formation was calculated from

¹ Richards and Jesse, *THIS JOURNAL*, 31, 277 (1910).

known data. Since the oxygen used contained only a small percentage of nitrogen, and because the bomb had been partially exhausted of air before oxygen was let in, this correction was very small. Its effect on the calorimeter approximated 0.0001° per centimeter of iron wire burned. All errors in the determination of this correction were quite negligible.

No further observations on the method and procedure are necessary. The notes of each experiment were recorded essentially in the manner detailed in a previous paper.¹

In order to effect economy of space in the following tabulation of results, the minor corrections, which depend upon the purely accidental nature of each particular experiment, are all algebraically added together in one column. The magnitudes of these corrections were about of the following order: Correction for calibration of the thermometer, $+0.013^{\circ}$; stirring, -0.015° ; for heat of combustion of wire, -0.018° . All these, together with the very small corrections for stem exposure and for nitric acid are included below in the column headed "Total corr." In all the tables except Table I, the rise of temperature due to the sugar taken to start the combustion (calculated from the outcome of Table I) is also included in this total correction.

The heat capacity of the system was increased 0.023% by slight alteration of the parts after the work described in Table VII; all subsequent work is corrected below, so as to reduce all to the original standard. The total heat capacity was equivalent to 2663.6 g. of water at first and 2664.2 later, as calculated from the rise of temperature caused by the combustion of sugar, assuming the Bureau of Standards' latest value (3945 cal. $[18^{\circ}]$ per gram weighed in vacuum) for the heat of combustion of the latter substance.²

The Quantitative Results and their Discussion.

TABLE I.—COMBUSTIONS OF CANE SUGAR (SUCROSE).³

| | Wt. sugar in vacuo. | Temperature range. | Observed rise in temp. | Total corr. | Corrected rise in temp. | Rise per gram sugar (weighed in vac.). |
|--------|------------------------|-----------------------|---------------------------|----------------|-------------------------------|--|
| 1..... | 2.00257 | 16.8–19.8 | 2.9870 | —0.0210 | 2.9660 | 1.4811 |
| 2..... | 2.00190 | 16.8–19.8 | 2.9855 | —0.0205 | 2.9650 | 1.4811 |
| 5..... | 2.00085 | 16.8–19.8 | 2.9885 | —0.0250 | 2.9635 | 1.4810 |
| 7..... | 2.0048 | 16.8–19.8 | 2.9910 | —0.0215 | 2.9695 | 1.4812 |
| 8..... | 2.0023 | 16.8–19.7 | 2.9850 | —0.0200 | 2.9650 | 1.4808 |
| 9..... | 1.93788 | 16.9–19.8 | 2.9010 | —0.0315 | 2.8695 | 1.4810 |

Average rise per gram sugar..... 1.4810°

Extreme variation from the mean..... 0.013%

¹ Richards, Henderson and Frevert, *Proc. Am. Acad.*, 42, 587 (1907).

² *Bull. Bur. Standards*, 11, 190 (1914) Paper 230.

³ NOTE.—The determinations recorded in Table I comprise all that were completed in a continuous series, save three. Of these, two, Nos. 4 and 6 in the continuous series,

The exceptionally close agreement of the values given in this table show how accurately it is possible to conduct experiments of this kind with the adiabatic calorimeter and the mercury thermometer. It will be noted that the temperature range was almost the same in each case, hence fundamental errors in the calibration of the thermometer could not appear. Of course, results as good as this can be expected on comparing different temperatures range only if the thermometer is everywhere thermodynamically consistent with itself, and this seems to be too much to expect of our present thermometric scale.¹

Feeling satisfied that the temperature rise during the combustion of sugar in our apparatus was hereby determined accurately enough for our purpose, we now proceeded to the thermally quantitative combus-

TABLE II.—BENZENE (A).

| Deter- mina- tion. | Wt. hydro- carbon in vacuo. G. | Wt. sugar in vacuo. G. | Final temp. | Obs. rise temp. | Total corr. | Corr. rise in temp. | Rise per g. hydro- carbon. |
|--------------------------------------|---|------------------------------|----------------|--------------------|----------------|------------------------|----------------------------------|
| 1..... | 0.79280 | 0.07040 | 19.8° | 3.097° | —0.123° | 2.974° | 3.751° |
| 2..... | 0.84505 | 0.10025 | 20.0 | 3.331 | —0.163 | 3.168 | 3.749 |
| 3..... | 0.91350 | 0.08870 | 20.3 | 3.576 | —0.149 | 3.427 | 3.751 |
| 4..... | 0.89805 | 0.09145 | 20.3 | 3.528 | —0.160 | 3.368 | 3.750 |
| 5..... | 0.72885 | 0.11175 | 19.9 | 2.923 | —0.189 | 2.734 | 3.752 |
| Average rise per gram benzene..... | | | | | | | 3.751°. |
| Extreme variation from the mean..... | | | | | | | 0.002° in 3.75° = 0.04% |

TABLE III.—TOLUENE.²

| | | | | | | | |
|--------------------------------------|---------|---------|-------|--------|---------|--------|-------------------------|
| 1..... | 0.81020 | 0.07970 | 20.0° | 3.225° | —0.133° | 3.092° | 3.817° |
| 2..... | 0.63535 | 0.41145 | 20.0 | 3.052 | —0.627 | 2.425 | 3.818 |
| 3..... | 0.80995 | 0.10140 | 20.2 | 3.252 | —0.160 | 3.092 | 3.817 |
| 4..... | 0.77820 | 0.08515 | 19.8 | 3.114 | —0.141 | 2.973 | 3.820 |
| 5..... | 0.85460 | 0.06145 | 20.0 | 3.358 | —0.098 | 3.260 | 3.815 |
| 6..... | 0.77370 | 0.07605 | 19.8 | 3.072 | —0.119 | 2.952 | 3.816 |
| 7..... | 0.74047 | 0.12570 | 19.8 | 3.023 | —0.197 | 2.826 | 3.817 |
| 8..... | 0.78500 | 0.08130 | 19.9 | 3.128 | —0.131 | 2.997 | 3.818 |
| Average rise per gram toluene..... | | | | | | | 3.8172° |
| Extreme variation from the mean..... | | | | | | | 0.003° in 3.82° = 0.08% |

Sample A was used in Nos. 6, 7, 8; Sample B, in Nos. 3, 4, 5; Sample C, in Nos. 1, 2.

were rejected because carbon or charcoal was discovered in the bomb after combustion. The other, No. 3 of the continuous series, was rejected because its temperature range was 1° lower than that of the others, and was such that the initial and final temperatures fell upon points that marked sharp and irregular changes in the slope of the curve of thermometric calibration.

¹ Richards and Thorvaldson, *THIS JOURNAL*, 37, 81 (1915).

² The above record comprises all the results in an unbroken series of completed determinations, save one. This omitted result yielded the value 3.8470 for the rise per gram toluene, which showed a variation from the average of the preceding of nearly 1%. Such a discrepancy, which corresponds to a thermometric error of 0.024° or to a weighing error of 0.006 g., is far beyond any possible variation resulting from experimental error; and must be due to misreading, probably of weights.

tion of the volatile hydrocarbons, the results for which are given in the following tables. In each of these experiments, as already stated, the hydrocarbon was enclosed in a small, hermetically sealed bulb and the combustion was started by means of a small amount of sugar. The temperature rise due to this sugar is included with the other smaller corrections in the column headed "Total corr." It was in each case obtained by simply multiplying the weight of sugar by the factor 1.481° , just found, according to Table I.

TABLE IV.—ETHYL BENZENE (A).

| Determination. | Wt. hydrocarbon in vacuo. G. | Wt. sugar in vacuo. G. | Final temp. | Obs. rise temp. | Total corr. | Corr. rise in temp. | Rise per g. hydrocarbon. |
|--|------------------------------|------------------------|-------------|-----------------|-------------|---------------------|--------------------------|
| 1..... | 0.83774 | 0.09761 | 20.3° | 3.398° | —0.167° | 3.231° | 3.857° |
| 2..... | 0.75158 | 0.11322 | 19.8 | 3.086 | —0.188 | 3.898 | 3.855 |
| 3..... | 0.67529 | 0.10992 | 19.8 | 2.792 | —0.189 | 2.603 | 3.855 |
| 4..... | 0.90187 | 0.07334 | 20.4 | 3.617 | —0.137 | 3.480 | 3.859 |
| 5..... | 0.90102 | 0.08665 | 20.4 | 3.625 | —0.151 | 3.474 | 3.856 |
| Average rise per gram ethyl benzene..... | | | | | | | 3.8565° |
| Extreme variation from the mean..... | | | | | | | 0.0025° in 3.86° = 0.06% |

TABLE V.—ETHYL BENZENE (C).

| | | | | | | | |
|---|---------|---------|-------|--------|---------|--------|----------|
| 1..... | 0.80760 | 0.13303 | 20.0° | 3.323° | —0.217° | 3.106° | 3.846° |
| 2..... | 0.77136 | 0.17095 | 20.1 | 3.240 | —0.273 | 2.967 | 3.847 |
| 3..... | 0.75198 | 0.17611 | 19.9 | 3.184 | —0.293 | 2.891 | 3.845 |
| Average rise per gram ethyl benzene..... | | | | | | | = 3.846° |
| Extreme variation from mean..... | | | | | | | = 0.001° |
| Correction for bromide present ¹ | | | | | | | = 0.008° |
| Corrected value..... | | | | | | | 3.854° |

TABLE VI.—MESITYLENE.

| | | | | | | | |
|---|---------|---------|-------|--------|---------|--------|-------------------------|
| 1..... | 0.94948 | 0.10076 | 20.2° | 3.856° | —0.169° | 3.687° | 3.883° |
| 2..... | 0.87078 | 0.09281 | 19.9 | 3.651 | —0.164 | 3.487 | 3.883 |
| 3..... | 0.95053 | 0.12873 | 20.1 | 3.900 | —0.211 | 3.689 | 3.881 |
| 4..... | 0.64775 | 0.13989 | 19.8 | 2.749 | —0.235 | 2.514 | 3.881 |
| 5..... | 0.92360 | 0.10692 | 20.1 | 3.767 | —0.181 | 3.586 | 3.883 |
| Average rise per gram mesitylene..... | | | | | | | 3.882° |
| Extreme variation from the mean..... | | | | | | | 0.001° in 3.88° = 0.03% |
| Sample A was used in Nos. 1 and 3; B, in Nos. 2 and 4; C, in No. 5. | | | | | | | |

TABLE VII.—PSEUDOCUMENE.

| | | | | | | | |
|--|---------|---------|-------|--------|---------|--------|--------------------------|
| 1..... | 0.92170 | 0.15390 | 20.4° | 3.829° | —0.258° | 3.571° | 3.875° |
| 2..... | 0.86005 | 0.11067 | 20.4 | 3.524 | —0.193 | 3.331 | 3.873 |
| 3..... | 0.99240 | 0.09866 | 20.5 | 4.001 | —0.160 | 3.841 | 3.871 |
| 4..... | 0.92585 | 0.10556 | 20.4 | 3.771 | —0.186 | 3.585 | 3.872 |
| Average rise per gram pseudocumene..... | | | | | | | 3.873° |
| Extreme variation from the mean..... | | | | | | | 0.002° in 3.873° = 0.05% |
| Sample A was used in 2, 3 and 4; Sample B, in 1. | | | | | | | |

¹ The washings of the bomb in one case yielded 4.9 mg. of silver bromide, corresponding to 2.84 mg. of ethyl bromide, the heat of combustion of a gram of which (according to Berthelot's figures) is 7.4 Calories less than that of a gram of ethyl benzene. Hence the correction to be applied is $0.00284 \times 7,400/2671 = 0.0078^\circ$.

TABLE VIII.—NORMAL PROPYL BENZENE.

| Determination. | Wt. hydro-carbon in vacuo. G. | Wt. sugar in vacuo. G. | Final temp. | Obs. rise temp. | Total corr. | Corr. rise in temp. | Rise per g. hydro-carbon. |
|---|-------------------------------|------------------------|-------------|-----------------|------------------------|---------------------|---------------------------|
| 1..... | 0.73741 | 0.14909 | 20.2° | 3.117° | -0.249° | 2.868° | 3.889° |
| 2..... | 0.91483 | 0.15620 | 20.4 | 3.817 | -0.260 | 3.557 | 3.888 |
| 3..... | 0.90782 | 0.16555 | 19.8 | 3.801 | -0.269 | 3.532 | 3.890 |
| Average rise per gram <i>N</i> propyl benzene..... | | | | | | | 3.889° |
| Corrected for change in heat capacity of calorimetric system (+0.023%)..... | | | | | | | 3.890° |
| Extreme variation from the mean..... | | | | | 0.001° in 3.9° = 0.02% | | |

TABLE IX.—ISOPROPYL BENZENE (A AND B).

| | | | | | | | |
|--|---------|---------|-------|--------|------------------------|--------|----------------------|
| 1..... | 0.82262 | 0.14734 | 20.2° | 3.445° | —0.243° | 3.202° | 3.892° |
| 2..... | 0.93195 | 0.16105 | 20.3 | 3.891 | —0.262 | 3.629 | 3.894 |
| 3..... | 0.87228 | 0.15930 | 20.3 | 3.651 | —0.257 | 3.394 | 3.891 |
| 4..... | 0.73131 | 0.19482 | 19.7 | 3.150 | —0.309 | 2.841 | (3.885) ¹ |
| 5..... | 0.82612 | 0.16830 | 20.3 | 3.483 | —0.277 | 3.206 | (2.881) ¹ |
| Average rise per gram isopropyl benzene, Sample A..... | | | | | | | 3.893° |
| Corrected for change in heat capacity of calorimetric system (+0.023%)..... | | | | | | | 3.894° |
| Extreme variation from the mean..... | | | | | 0.002° in 3.9° = 0.05% | | |
| Sample A was used in Nos. 1, 2 and 3; Sample B, in Nos. 4 and 5. | | | | | | | |

TABLE X.—TERTIARY BUTYL BENZENE.

| | | | | | | | |
|--|---------|---------|-------|--------|---------|--------|--------|
| 1..... | 0.89891 | 0.18351 | 20.0° | 3.814° | -0.297° | 3.517° | 3.912° |
| 2..... | 1.07954 | 0.18321 | 20.4 | 4.517 | -0.294 | 4.224 | 3.913 |
| 3..... | 1.01951 | 0.15835 | 20.4 | 4.250 | -0.258 | 3.992 | 3.916 |
| Average rise per gram III butyl benzene..... | | | | | | | 3.913° |
| Corrected for change in heat capacity of system (+0.023%) | | | | | | | 3.914° |
| Extreme variation from the mean..... | | | | | | | 0.06% |

TABLE XI.—CYCLOHEXANE.

| | | | | | | | |
|--|---------|---------|-------|--------|---------|--------|---------|
| 1 ² | 0.92870 | 0.13580 | 20.2° | 4.090° | -0.222° | 3.868° | (4.165) |
| 2..... | 0.62918 | 0.09031 | 19.8 | 2.797 | -0.160 | 2.637 | 4.192° |
| 3 ³ | ... | ... | .. | .. | .. | .. | 4.189 |
| Mean of 2 and 3..... | | | | | | | 4.190° |
| Corrected for change in heat capacity (+0.023%)..... | | | | | | | 4.191° |
| Extreme variation..... | | | | | | | 0.07% |

The study of the individual results in this long series of determinations shows that, although the results are sometimes not quite so concordant

¹ Sample B of isopropyl benzene, made by the Grignard reaction, was doubtless less pure than A, made by the Friedel and Crafts reaction. Accordingly the results with Sample B are not included in the average.

² The result of determination 1 (made in Sample B) is not included in the average. Hexamethylene B contained more benzene than hexamethylene A, which was used in Nos. 2 and 3.

³ Immediate data mislaid at date of writing. It is known, however, that the measurement involved very closely the same temperature range.

as those with the sugar alone, they are, nevertheless, as closely concordant as the circumstances permit. In most cases the extreme variation from the mean is less than 0.002° in the final results, while in many cases the agreement is even better than this; and in no case do the variations cause the highest result with one isomer to overlap the lowest result with the isomer giving the larger output of heat. As regards the different preparations of substance, the discrepancy between the two samples of ethyl benzene has already been noted, and its cause explained. Unquestionably the samples of ethyl and isopropyl benzene, labeled *A*, purer than those labeled *B*, and the excellent results obtained with them will be used in the future discussion. As against this discrepancy it is interesting to note that in the cases of toluene, mesitylene, and pseudocumene, the different samples gave almost identical results in each case. This is doubtless because the impurities in these preparations were chiefly homologous hydrocarbons, which would have much less effect upon the heat of combustion than upon the boiling points that served as the criterion of purity. This comparison is especially instructive as showing the different effect of different kinds of impurities.

Let us now collect all these results for the rise of temperature caused by the combustion of one gram of these several hydrocarbons in a systematic table, and reduce the data to the usual standards, in the first place giving the ratio of the rise of temperature caused by each substance to that caused by exactly one gram of sugar, and in the next place giving the corresponding absolute value for the heat of combustion of one gram of each substance, based on the current absolute values for the heat of combustion of sugar.

Unfortunately the absolute value for the heat of combustion of sugar is not agreed upon by all authorities. The best of the earlier work has been done by Fischer and Wrede, who found as the absolute value 16.545 kilojoules (or kilowatt seconds).¹ A very careful study of the data concerning the mechanical equivalent of heat by Professor Harvey N. Davis, of Harvard, indicates that at 16° this is 4.1846, and at 20° 4.1800. Therefore, accepting this estimate, we may decide that the value over the range used in these experiments is closely 4.182, that is to say, one joule equals 0.23912 calorie. On this basis Fischer and Wrede's value for the heat of combustion of sugar becomes 3956 calories per gram.

On the other hand, the most recent work of the Bureau of Standards of Washington, published by Dickinson,² seems to have been very carefully performed, and to be worthy to supersede the German work. The value here given is 3949 calories (20°) per gram sugar weighed in air, or 3947 calories per gram weighed in vacuum. In 18° -calories this latter figure

¹ Fischer and Wrede, *Sitzb. kgl. preuss. Akad.*, 5, 145 (1908).

² *Bull. Bur. Stand.*, 11, 190 (July, 1914)

would become 3945. In the table below, the value given by the Bureau of Standards is used, but anyone preferring the other (Fischer and Wrede's) can easily add to each value 0.28%.

In the table below there are included also the results concerning xylenes obtained by one of us in collaboration with R. H. Jesse,¹ because this formed an integral part of the series. With these preliminaries the summarized table of results may be given:

TABLE XII.—SUMMARY OF DATA AND SPECIFIC HEAT OF COMBUSTION.

| | Rise of temp. caused by 1,000 g. substance. | Ratio of this rise to that caused by 1,000 g. sugar. | Absolute heat of combustion of 1 g. Calories (18°). Kilojoules. | |
|---|---|--|---|----------|
| Sucrose (Standard)..... | 1.4810° | (1.0000) | (3.945) | (16.498) |
| Benzene (C ₆ H ₆)..... | 3.751 | 2.533 | 9.993 | 41.79 |
| Toluene (C ₇ H ₈)..... | 3.817 | 2.577 | 10.166 | 42.51 |
| Ethyl benzene A..... | 3.857 | 2.604 | 10.273 | 42.96 |
| Xylene ortho (R. & J.)..... | ... | 2.605 | 10.277 | 42.98 |
| Xylene meta (R. & J.)..... | ... | 2.605 | 10.277 | 42.98 |
| Xylene para (R. & J.)..... | ... | 2.596 | 10.241 | 42.83 |
| Mesitylene C ₉ H ₁₂ | 3.882 | 2.621 | 10.340 | 43.24 |
| Propyl benzene (normal)..... | 3.890 | 2.627 | 10.364 | 43.34 |
| Isopropyl benzene (cumene)..... | 3.893 | 2.629 | 10.371 | 43.37 |
| Pseudocumene..... | 3.873 | 2.615 | 10.316 | 43.14 |
| Tertiary butyl benzene..... | 3.914 | 2.643 | 10.427 | 43.60 |
| Hexamethylene (cyclohexane)..... | 4.191 | 2.830 | 11.164 | 46.69 |

On comparing these results with the earlier results of others, it is noticeable, first, that the value for benzene is slightly lower than that found by Richards and Jesse five years ago, their value having been 2.538 instead of 2.533 times that of sugar. Nevertheless, our value as given below is decidedly higher than that found earlier by Richards, Henderson and Frevert, and recognized by them as having been too low because of incomplete combustion. The manner of experiment, excepting small details, was very similar in our case to that in the case of Richards and Jesse, and the difference of 0.2%—a quantity distinctly greater than the error of experimentation—needs further elucidation. The matter is, in fact, being studied further in the Wolcott Gibbs laboratory, and it is hoped that before long more light upon it may be obtained. It is possible, indeed, probable, judging from the variations among the Harvard results and also from the varying results obtained by others,² that the complete

¹ Richards and Jesse, *THIS JOURNAL*, 31, 294 (1910).

² See W. A. Roth's able discussion of this subject in the Landolt-Börnstein Tables, page 910, 1912. Roth used the factor 4.189 for the conversion of kilojoules to calories. Accordingly his figures are slightly different from ours as given above. Attention should be called to the error in the next to the last and the preceding column on that page. Instead of "const. vol." and "g. Kal pro gram" the headings should read "Konst Druck" and "Konst. vol.," respectively, like the corresponding columns on p. 911. Roth's work is very thorough and painstaking. In this connection, attention

combustion of benzene in the bomb is a difficult matter, and although the method adopted in the Harvard work has probably secured the best combustion heretofore attained, there is good reason to believe that the further treatment by passing the gases remaining in the bomb over a hot catalyzer is necessary in the case of a substance as volatile as benzene. This has, in fact, been done in a yet more recent research by one of the authors, helped by Dr. H. S. Davis, and before long the further results of this research will be communicated. The same objection does not apply so seriously to the higher boiling liquids, where the vaporization is less rapid and the chance for the escape of unburned carbon monoxide is much less.

Our results also for toluene are higher than those of Roth, and of ethyl benzene, higher than those of Jesse.¹ It is probable that less trouble was taken to dry the substances than in our case, and possibly also our combustion was more complete. For cyclohexane, our results are above those of Roth and below those of Zubow, who found respectively 11127 and 11231 for the heat of combustion of a gram,² instead of our value 11164.

On the other hand, our value for normal propyl benzene is somewhat below that given by Genvresse. All these results and others are recorded in Roth's recalculation, already quoted.

Incidentally it should be noted that these values, as given by the combustion of the material in a closed bomb, correspond to the reaction in constant volume.

It is now a matter of much interest to record these results in the usual standard, namely, in terms of the gram molecule. The molal heats of combustion are, of course, very easily calculated from the specific heats of combustion by multiplying in each case by the appropriate molecular weight.

This table is very interesting from many points of view. In the first place, the striking similarity of the heats of combustion of isomers is distinctly shown. In the eight-carbon isomers recorded above (of which there are four), the range is only between 4559 and 4543 kilojoules, a difference of only $\frac{1}{3}$ of one per cent.; and in the case of the nine-carbon isomers, the range is not much greater, extending only from 5180 to 5208 kilojoules, a difference of a little over 0.5%. The increase of molal heat of combustion, due to the addition of CH_2 , remains nearly constant throughout the series. Between benzene and toluene it is 651 kilojoules; should be called to the interesting and comprehensive paper entitled "Thermochemische Untersuchungen," by W. A. Roth and Auwers, which has reached us too late for discussion here. The new values found by them for benzene, toluene and cyclohexane are very near ours (*Lieb. Ann.*, 407, 109 (1914)).

¹ R. H. Jesse, Jr., *THIS JOURNAL*, 34, 1340 (1912).

² See Landolt-Börnstein (1912).

between toluene and ethyl benzene, 644; between ethyl benzene and propyl benzene, 647; between propyl benzene and butyl benzene, 643—the average being 646. It is possible that the true average is slightly less than this, because the value of benzene given above may be slightly too low, as already stated.

TABLE XIII.—MOLAL HEATS OF COMBUSTION.

| Formula. | Mol. wt. C = 12.000. H = 1.0078. | Absolute heat of combustion (in const. vol.) of 1 mol. | |
|---|--|---|-------------|
| | | Calories (18°). | Kilojoules. |
| Benzene, C_6H_6 | 78.05 | 780.0 | 3262 |
| Toluene, $C_6H_5CH_3$ | 92.06 | 935.9 | 3913 |
| Ethylene benzene, $C_6H_4C_2H_4$ | 106.08 | 1089.8 | 4557 |
| Xylene (<i>o</i>), $C_6H_4(CH_3)_2$ | 106.08 | 1090.2 | 4559 |
| Xylene (<i>m</i>), $C_6H_4(CH_3)_2$ | 106.08 | 1090.2 | 4559 |
| Xylene (<i>p</i>), $C_6H_4(CH_3)_2$ | 106.08 | 1086.4 | 4543 |
| Mesitylene, $C_6H_3(CH_3)_3$ | 120.09 | 1241.7 | 5193 |
| Propyl benzene (<i>n</i>), $C_6H_5C_3H_7$ | 120.09 | 1244.6 | 5204 |
| Isopropyl benzene, $C_6H_5CH(CH_3)_2$ | 120.09 | 1245.5 | 5208 |
| Pseudocumene, $C_6H_3(CH_3)_3$ | 120.09 | 1238.8 | 5180 |
| Butyl benzene (tert.), $C_6H_5C(CH_3)_3$ | 134.11 | 1398.4 | 5847 |
| Cyclohexane, C_6H_{12} | 84.09 | 938.8 | 3926 |

The data are not yet plentiful enough to permit definite conclusions as to the effect of the more subtle features of the grouping upon the heat of combustion.

The six extra atoms of hydrogen in cyclohexane evolve 564 kilojoules upon burning as compared with benzene. The same amount of hydrogen gas would have evolved half again as much, but, of course, the situation is so complex that an exact interpretation of differences of this sort is as yet beyond our reach. It is hoped that this work may be continued, and not only further progress made with regard to compounds of this type, but also that the work may be extended to other compounds, so as to secure a great variety of accurate data upon which conclusions concerning the total energy relations of organic substances may be built. This is especially important, because, as is well known, many of Thomsen's carefully obtained data are vitiated by the defect of his "universal burner," and in many of the earlier results obtained from the bomb, the combustion was undoubtedly incomplete.

In concluding, we are glad to express our indebtedness to Dr. G. L. Kelley for generous assistance in developing the methods adopted and in directing an assistant employed in preparing and purifying some of the higher homologs; and also to the Carnegie Institution of Washington for the subsidy which alone has made the investigation possible.

Summary.

The principal results of this investigation may be summarized as follows:

1. The method of adiabatic calorimetry as applied to combustion in the Berthelot bomb has been further improved in several directions, making more accurate determinations possible.

2. The agreement among the results with any substance is close enough to show that the method is capable of all the necessary refinement.

3. The relative heats of combustion of sugar, benzene, toluene, ethyl benzene, normal and isopropyl benzene, mesitylene, pseudocumene and cyclohexane have been determined.

4. The striking similarity between the heats of combustion of various isomers appears. Nevertheless, real differences exist, and will doubtless some time, when more data are available, be capable of reference to differences in molecular stability and configuration.

5. The boiling points of these liquids have been carefully studied, especially those of exceptionally pure toluene (110.31°) and cyclohexane (80.8°); and the melting point of benzene also has been determined as 5.484° , while that of cyclohexane was found to be 5.97° .

CAMBRIDGE, MASS., 1911-1912; 1915.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF LEAD. THE ANALYSIS OF LEAD BROMIDE.

[SECOND PAPER.]

BY GREGORY PAUL BAXTER AND THORBERGUR THORVALDSON.

Received March 8, 1915.

Since the work by Baxter and Wilson¹ on the atomic weight of lead by the analysis of lead chloride some years ago, which yielded the value 207.09 ($\text{Ag} = 107.880$), the atomic weight of lead has been under almost continuous investigation in the Harvard Laboratory. Attempts were made by Mr. W. A. Worsham to synthesize the sulfate from the metal, but serious difficulties were met in the production of lead sulfate free from occluded matter, and in the drying of the sulfate, so that this method was temporarily given up in favor of the analysis of lead bromide. The latter substance, in spite of the fact that it is somewhat less soluble than lead chloride, is, nevertheless, sufficiently soluble for the purpose. Preliminary experiments in the preparation of pure lead bromide were carried out by Mr. Worsham. The investigation was then continued by the present authors, and finally was taken up by Mr. F. L. Grover. This paper presents the results of Dr. Thorvaldson's experiments, while the following one describes the completion of the research by Mr. Grover.

The method employed was the usual one in the case of metallic halides, with special modifications made necessary by the idiosyncrasies of lead

¹ *Proc. Amer. Acad.*, 43, 365 (1907); *THIS JOURNAL*, 30, 187 (1908); *Z. anorg. Chem.*, 57, 174 (1908).

bromide. Weighed amounts of the salt, which had been fused in an atmosphere containing hydrobromic acid, were dissolved in hot water which had been slightly acidified. To the solution after cooling was added a solution of a weighed, very nearly equivalent, amount of metallic silver. Any deficiency of bromide or silver was then added in the form of very dilute standard solutions, so that the exact amount of silver required could be accurately estimated. Finally, the silver bromide was collected and weighed.

The Purification of Materials.

Water, nitric acid and ammonia were purified by distillation in the usual fashion.

Hydrobromic Acid.—At first hydrobromic acid was prepared as explained in the paper by Baxter, Thorvaldson and Cobb upon the analysis of ferrous bromide.¹ This acid was made from bromine which had been freed from chlorine by distillation from aqueous potassium bromide (Sample I). The hydrobromic acid was synthesized by saturating hydrogen with bromine and conducting the mixed gases over hot platinum. The hydrogen was made from "hydrone" and was purified by scrubbing and passing over stick potassium hydroxide. The acid gas was collected in water and the solution was purified by distillation. Material produced in this way still gave evidence of containing organic matter,² so that for the later preparations steps were taken to free the bromine from such impurities by converting it to potassium bromide and fusing the salt with potassium permanganate, as described in detail in the following paper. From this potassium bromide, bromine was set free by adding three-fourths of the theoretical quantity of potassium permanganate and sulfuric acid. In this way the bromine received still a third distillation from a bromide (Sample II). The product was converted into hydrobromic acid by direct combination with pure hydrogen in contact with platinum. The gas was collected in the purest water, and the solution distilled, with rejection of the extreme fractions.

Lead Bromide.—This substance was prepared by precipitation of lead nitrate with hydrobromic acid solution, and crystallization of the product by solution in hot concentrated hydrobromic acid and reprecipitation by diluting the solution with water.

Sample A consisted of residues from earlier work by Mr. Worsham, which were recrystallized from hydrobromic acid solution, as above, with centrifugal drainage. The material was somewhat blackened at the outset but was pure white after crystallization.

¹ THIS JOURNAL, 33, 326 (1911); *Z. anorg. Chem.*, 70, 329 (1911).

² This organic matter may have originated partly in the hydrogen made from hydrone. Baxter and Hoover, THIS JOURNAL, 34, 1659 (1912); *Z. anorg. Chem.*, 80, 203 (1913).

The source of Sample B was lead nitrate which had been purified by Dr. J. W. Shipley. The method of purifying the nitrate consisted in precipitating lead sulfate and washing this substance very thoroughly, converting it into lead sulfide by contact with a saturated solution of hydrogen sulfide, and solution in pure nitric acid. Three recrystallizations as nitrate followed, the mother liquors of the last two crystallizations being found free from sulfate. The nitrate was dissolved in water in a quartz dish and a slight excess of dilute hydrobromic acid was added. The crystals were separated from the mother liquor by centrifugal drainage in platinum Gooch crucibles, and were thoroughly rinsed with water. The lead bromide was dissolved in constant boiling hydrobromic acid in a quartz dish and again precipitated by dilution with water. Centrifugal drainage and rinsing followed. After a second recrystallization a portion of the material was reserved for analysis, Sample B₁. The remainder was once again recrystallized, Sample B₂.

Sample C was prepared from lead nitrate which, in turn, was obtained from precipitated lead chloride. The latter substance, after thorough washing, was changed to sulfide as above. The sulfide was washed and dissolved in nitric acid, and the lead nitrate was recrystallized three times. The preparation of lead bromide from this nitrate followed the lines indicated in the case of Sample B. Sample II of bromine was used.

Sample D. Lead nitrate for the preparation of this sample was obtained by recrystallizing the commercial product five times from nitric acid and once from aqueous solution. The bromide was prepared as above with Sample II of bromine.

The final crystallizations of the lead nitrate were carried out in platinum or quartz vessels, while the preparation and crystallization of the lead bromide was always conducted in quartz vessels. A quartz condenser was used for the distillation of the hydrobromic acid, and the distillate was collected in quartz vessels.

Silver.—Pure silver was prepared as frequently described in papers from the Harvard Chemical Laboratory. The particular specimen used in this work had already been used in the investigation upon ferrous bromide¹ (Sample A).

Preparation of Lead Bromide for Analysis.

The drying of lead bromide was effected by fusion in a dry atmosphere containing a considerable proportion of hydrobromic acid gas. In the earlier experiments the apparatus was identical with that used in the research upon ferrous bromide. Fuming hydrobromic acid gas was made by passing the synthetic gas into ice-cold water. A slight excess of bromine was removed by adding a small amount of ferrous bromide. Pure nitrogen was then bubbled through this solution, thereby acquiring a very consider-

¹ Baxter, Thorvaldson and Cobb, *Loc. cit.*

able hydrobromic acid content, and the mixture was dried by passing it over fused calcium bromide.¹ The lead bromide, contained in a platinum boat, which in turn was placed in the quartz tube of a "bottling apparatus,"² was heated in a current of nitrogen and hydrobromic acid, gently at first, so that the greater part of the moisture in the salt was expelled at a low temperature, later at gradually increasing temperatures until finally fusion took place. The bottling apparatus and tube, after the salt had been allowed to cool, were then swept out with a current of pure nitrogen, and this in turn was displaced with dry air. Thereupon the boat and contents, by means of the bottling apparatus, were transferred to the weighing bottle, without exposure to moisture.

When lead bromide, fused as above, is treated with water, either cold or warm, a clear solution is never obtained. The horny mass of fused material whitens superficially, and if the solution is boiled, a white precipitate appears. At first the difficulty was ascribed to hydrolysis of the salt during fusion, but no precautions as to the preliminary drying of the salt before fusion, so as to insure fairly complete elimination of the water, produced any difference in the result, so that the conclusion was reached that the difficulty is caused by hydrolysis during solution. So far as obtaining a clear solution of the salt is concerned, a simple remedy was found in acidifying the solution slightly. In the experiments described in this paper, acetic acid was used for the purpose, although in the work described in the following paper a small amount of nitric acid was found to be equally satisfactory. It was necessary, however, to obtain further evidence as to the cause of the difficulty. This was done as follows: Neutral lead bromide, precipitated by the addition of a solution of recrystallized potassium bromide to a solution of recrystallized lead nitrate, was thoroughly washed by decantation and centrifugally drained. Three grams of this lead bromide when heated with about 600 cc. of water dissolved partially, leaving, however, a considerable amount of white insoluble matter, which did not dissolve when the solution was replaced by a liter of water. Fearing that the lead bromide which served as the starting point of this experiment might have been slightly basic, the experiment was repeated with material which had been crystallized from slightly acid solution. Even here the salt did not give a clear solution, a similar white insoluble residue remaining. Thus, material which surely must have been initially neutral or acid behaved, so far as we could tell, as the fused material behaved. In order to discover whether the insoluble matter is basic bromide or hydroxide, some of it was washed thoroughly, dissolved in nitric acid and treated with silver nitrate. A precipitate of

¹ Baxter and Warren found calcium bromide to be a very efficient drying agent, *THIS JOURNAL*, 33, 340 (1911).

² Richards and Parker, *Proc. Amer. Acad.*, 32, 59 (1896).

silver bromide was produced, indicating the insoluble substance to be a basic bromide. In still another experiment some of the lead bromide which had been prepared from neutral potassium bromide and lead nitrate was dried in a current of hydrobromic acid at a temperature nearly as high as the fusion point. This material also yielded an insoluble residue. Since there seemed, therefore, to be reason to believe that lead bromide fused in an atmosphere containing hydrobromic acid is not basic, the analyses of the fused material were next carried out.

Before doing so, however, it was necessary to prove that during the solution of the bromide in the dilute acetic acid solution no volatile compounds of bromide are lost. About 4 g. of lead bromide were placed in a distilling flask with 400 cc. of water and 5 cc. of acetic acid, that is, ten times as much acetic acid was used as was ever used in an analysis. The solution was distilled and the distillate was collected and tested for bromide with silver nitrate. In the test portion about 0.004 mg. of bromine was found. Since the solution was more concentrated in lead bromide and since far more acetic acid was used than in any of the analyses, and since in practice the solution was never actually boiled while the lead bromide was dissolving, it seemed certain that the danger of losing bromine was negligible.

Even when the lead bromide was dissolved in acidulated water, there remained always a slight black residue, which was never observed when unfused material was dissolved. In later work by Mr. Grover and Dr. Hartmann in this laboratory it was found that this black residue consists in part of carbon formed by the charring of organic impurities, and in part of silicic acid, extracted probably from the quartz dishes. The proportion of this material was diminished when the hydrobromic acid was prepared from the purest bromine as previously described, but no specimen of fused material was ever obtained absolutely free from it. In this research the residue was very carefully examined for lead with negative results, and in the work described in the following paper evidence was obtained as to its real nature. From evidence obtained in the later research it seems probable that the weight of this black residue amounted to about 0.004%. This proportion would raise the observed atomic weight of lead by 0.015 unit in the comparisons with silver only, since it must have been collected and weighed with the silver bromide which is only slightly heavier than the lead bromide.

In order to dissolve the lead bromide, the boat after being weighed was transferred to a large Jena glass flask and was covered with nearly a liter of the purest water, to which about 0.5 cc. of glacial acetic acid was added. The solution was then heated almost to the boiling point until the lead bromide had dissolved. This required several hours. Next a quantity of the purest silver, very nearly equivalent to the lead bromide, was weighed

out and dissolved in nitric acid and this solution also was diluted to a total volume of about a liter. The lead bromide solution was transferred quantitatively to a glass-stoppered precipitating flask, and, both solutions being cold, the silver nitrate solution was slowly poured into the lead bromide solution. The solutions were then thoroughly mixed by shaking and allowed to stand with occasional shaking for a few days. Next the liquid was examined in a nephelometer for excess of bromide or silver, and any deficiency of either was made up by the addition of 0.01*N* silver or bromide solution. Usually the comparison was completed within ten days of the time of precipitation, but in two analyses, 5 and 6, the precipitates were left under the solution for about four weeks longer. No perceptible alteration in end point during this period could be observed. As soon as the exact end point had been found, a slight excess of silver nitrate was added and the silver bromide was washed and collected upon a platinum-sponge Gooch crucible. After being dried for several hours at about 180° the silver halide was weighed. Residual moisture was determined by the loss in weight on fusion in a porcelain crucible, and a correction for solubility of the silver bromide in the wash-water of 0.1 mg. per liter of water was applied.

The silver bromide from one experiment was tested for occluded lead salts by solution in potassium cyanide, reprecipitation with hydrochloric acid, evaporation of the solution and addition of (A) hydrogen sulfide, (B) sulfuric acid. The evidence was negative.

In the first five analyses the hydrobromic acid gas mixture was produced as described above, but since we still feared that the fused salt might be basic, in subsequent analyses the concentration of hydrobromic acid was considerably increased. This was done by using synthetic gas produced as in the apparatus employed by Richards and Hönigschmid in their work upon the atomic weight of calcium.¹ This hydrobromic acid was formed by saturating hydrogen gas with the purest bromine at a temperature in the neighborhood of 44° and passing the mixed gases over hot platinum. The hydrobromic acid gas contained a slight excess of hydrogen. It was dried by fused calcium bromide. During the fusion of the lead bromide a small amount of nitrogen was passed into the apparatus, but even then the concentration of the hydrobromic acid must have been far greater than in the earlier experiments.

The effect of this change in procedure was not to increase, but, on the whole, to diminish slightly the apparent proportion of bromine in the salt, but it is by no means certain that the slight differences were really caused by the change in the process of fusion, since the earlier analyses were naturally subject to the uncertainties of preliminary determinations.

The platinum boat did not remain absolutely constant in weight, but

¹ THIS JOURNAL, 32, 1583 (1910).

lost by amounts varying from 0.1 to 0.3 mg. in each analysis. No correction was applied for the change, which averaged -0.14 mg.

Vacuum corrections were applied as follows:

| | Specific gravity. | Vacuum correction. |
|---------------------|-------------------|--------------------|
| Weights..... | 8.3 | |
| Silver..... | 10.49 | -0.000031 |
| Silver bromide..... | 6.473 | $+0.000041$ |
| Lead bromide..... | 6.66 | $+0.000035$ |

SERIES I.

| Ag = 107.880. | | PbBr ₂ : 2Ag. | | Br = 79.916. | | | |
|---------------------|-------------------------------|--|-----------------------------|------------------------|-----------------------------------|--------------------------------|----------------|
| Number of analysis. | Sample of PbBr ₂ . | Wt. of PbBr ₂ in vacuum. Grams. | Wt. of Ag in vacuum. Grams. | Wt. of Ag added. Gram. | Corr. wt. of Ag in vacuum. Grams. | Ratio PbBr ₂ : 2Ag. | At. wt. of Pb. |
| 1 | A | 6.55858 | 3.85650 | -0.00040 | 3.85610 | 1.70083 | 207.14 |
| 2 | B ₁ | 4.83285 | 2.84146 | -0.00020 | 2.84126 | .70095 | 207.17 |
| 3 | B ₂ | 5.67758 | 3.33797 | -0.00010 | 3.33787 | .70096 | 207.17 |
| 4 | B ₂ | 6.73361 | 3.95874 | 0.00000 | 3.95874 | .70095 | 207.16 |
| 5 | B ₂ | 5.93130 | 3.48710 | -0.00050 | 3.48660 | .70117 | 207.21 |
| 6 | B ₂ | 5.01729 | 2.94948 | $+0.00020$ | 2.94968 | .70096 | 207.17 |
| 7 | C | 5.89902 | 3.46810 | -0.00080 | 3.46730 | .70133 | 207.25 |
| 8 | C | 7.71526 | 4.53568 | -0.00070 | 4.53498 | .70128 | 207.24 |
| 9 | C | 7.40244 | 4.35147 | $+0.00010$ | 4.35157 | .70110 | 207.20 |
| 10 | D | 7.01144 | 4.12204 | -0.00050 | 4.12154 | .70117 | 207.21 |
| 11 | D | 6.91460 | 4.06454 | $+0.00030$ | 4.06484 | .70108 | 207.19 |
| 12 | D | 8.12623 | 4.77699 | -0.00020 | 4.77679 | .70119 | 207.22 |
| Average, | | | | | | 1.70108 | 207.19 |

SERIES II.

| | | PbBr ₂ : 2AgBr. | | | | | | |
|---------------------|-------------------------------|--|-------------------------------|-------------------------------------|-----------------------|-------------------------------------|----------------------------------|----------------|
| Number of analysis. | Sample of PbBr ₂ . | Wt. of PbBr ₂ in vacuum. Grams. | Wt. of AgBr in vacuum. Grams. | Wt. of AgBr from wash waters. Gram. | Loss on fusion. Gram. | Corr. wt. of AgBr in vacuum. Grams. | Ratio PbBr ₂ : 2AgBr. | At. wt. of Pb. |
| 13 | A | 6.55858 | 6.71235 | 0.00024 | 0.00018 | 6.71241 | 0.97708 | 207.15 |
| 14 | B ₂ | 6.73361 | 6.89146 | 0.00015 | 0.00037 | 6.89124 | 0.97713 | 207.17 |
| 15 | B ₂ | 5.01729 | 5.13422 | 0.00017 | 0.00039 | 5.13400 | 0.97727 | 207.22 |
| 16 | C | 7.71526 | 7.89593 | 0.00015 | 0.00082 | 7.89526 | 0.97720 | 207.20 |
| 17 | D | 7.01144 | 7.17509 | 0.00013 | 0.00052 | 7.17470 | 0.97725 | 207.21 |
| 18 | D | 6.91460 | 7.07689 | 0.00022 | 0.00039 | 7.07672 | 0.97709 | 207.16 |
| Average, | | | | | | 0.97717 | 207.19 | |

Average of Series I and II, 207.19

It is obvious that the foregoing data indicate a value for the atomic weight of lead decidedly above the earlier one found by Baxter and Wilson, although that in turn was nearly 0.3 unit higher than the one commonly accepted at the time. Even in the case of an atomic weight as high as that of lead, the difference is larger than the experimental error. The investigation was therefore continued by Mr. F. L. Grover, whose work

with both lead bromide and lead chloride is described in the following paper.

We are very greatly indebted to the Carnegie Institution of Washington for generous assistance in pursuing this investigation.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF LEAD. THE ANALYSIS OF LEAD BROMIDE AND CHLORIDE.

[THIRD PAPER.]

BY GREGORY PAUL BAXTER AND FRANK LESLIE GROVER.

Received March 8, 1915.

CONTENTS.

INTRODUCTION: Part I: THE ANALYSIS OF LEAD BROMIDE. Purification of Reagents; Purification of Lead Nitrate; Preparation of Lead Bromide; Drying of Lead Bromide for Analysis; Analysis of the Lead Bromide; Results and Discussion.

Part II: THE ANALYSIS OF LEAD CHLORIDE. The Purification of Lead Nitrate; The Radioactivity of the Minerals; The Purification of Lead Chloride; The Drying of Lead Chloride; The Neutrality of Fused Lead Chloride; The Analysis of Lead Chloride; Results and Discussion.

Introduction.

The outcome of the investigation described in the preceding paper, that the atomic weight of lead is nearly 207.2, rather than 207.1 as previously found by Baxter and Wilson,¹ led us to pursue the subject further with the greatest care, in order if possible to discover the cause of the difference, and at any rate to come to a definite conclusion as to the real value of the constant in question. In the first place, it was conceivable, in spite of the evidence obtained, that the lead bromide which had been fused in hydrobromic acid was slightly basic. In the second place, recently the apparent relationship of lead to radioactive change has aroused interest as to the identity of lead from different sources, and suggested the possibility that the lead material used by Baxter and Thorvaldson was different from that used earlier by Baxter and Wilson. These points were carefully tested. In the first place, lead bromide was prepared with even greater pains than before, and analyzed. Since this work yielded evidence in accord with the results given in the preceding paper, lead chloride was then investigated anew, with the outcome that essentially the same result was obtained as with the bromide, namely, 207.2.

While this investigation was in progress, the exact value of the atomic weight of lead became of considerable importance in connection with the theory of atomic disintegration of the radioactive elements. According

¹ *Proc. Amer. Acad.*, 43, 365 (1907); *THIS JOURNAL*, 30, 187 (1908).

to the hypothesis of Fajans¹ and Soddy² at least two lead "isotopes" exist, one resulting from the expulsion of five α -particles from radium with an atomic weight 206, the other resulting from the expulsion of eight α -particles from thorium with an atomic weight of about 208.3. If ordinary lead is composed of, or contains, these isotopes, in proportions varying with its origin, then its atomic weight might be expected to vary according to its source. Richards and Lambert³ found that, in accordance with this hypothesis, radioactive lead extracted from radioactive minerals possesses an atomic weight different from that of ordinary lead, and differing also according to the mineral from which it is extracted, a result confirmed by Hönigsmid,⁴ M. Curie⁵ and Soddy.⁶ In order to find out whether ordinary lead is subject to similar variations, seven varieties of inactive lead material from known widely different geographical sources were examined. Not the slightest difference between any of these specimens could be detected so far as analysis of the chloride is concerned. Furthermore these specimens were found to be spectroscopically identical and none of them were radioactive, so far as could be determined. While the evidence thus obtained is by no means final as to the origin of ordinary lead, it certainly is striking that, if common lead is composed either wholly or in part of isotopes, its composition should be essentially constant.

PART I. THE ANALYSIS OF LEAD BROMIDE.

Purification of Reagents.

General reagents were purified by methods found amply satisfactory in the past.

Water.—All the pure water used in this work was prepared by double distillation, once from alkaline permanganate, and once from very dilute sulfuric acid. The condensers were block-tin tubes, fitted to Jena flasks with constricted necks, which served as stills. The connection was made by a water seal, no rubber or cork being used. The water was collected in Jena flasks or non-sol bottles, generally just previous to use.

Ammonia.—The concentrated C. P. reagent was gently boiled in a ground-stoppered flask, and the gas conducted through a glass tube to the surface of the purest water.

Nitric Acid.—Concentrated C. P. nitric acid was distilled through either a quartz or platinum condenser, with rejection of the first two-thirds of the distillate. The last third was collected in a quartz flask. The purity of nitric acid distilled through either platinum or quartz

¹ *Ber.*, 46, 422 (1913).

² *Chem. News*, 107, 97 (1913).

³ *THIS JOURNAL*, 36, 1329 (1914).

⁴ *Compt. rend.*, 158, 1786 (1914); *Z. Elect.*, 20, 319.

⁵ *Ibid.*, 158, 1676 (1914).

⁶ *Proc. Chem. Soc.*, 30, 134 (1914).

has been several times investigated in the past, but recently we made this matter the subject of a special investigation,¹ and found no evidence that well cleaned platinum vessels are affected by nitric acid.

Bromine.—Crude bromine was subjected to the following treatment in order to remove chlorine, iodine, and organic matter. Special pains were taken to eliminate the last impurity, because of the difficulty met by Baxter and Thorvaldson in preparing lead bromide free from organic matter. The treatment used was essentially that employed by Baxter, Moore, and Boylston² in an investigation upon the atomic weight of phosphorus.

The crude material was first subjected to distillation from aqueous potassium bromide in order to remove chlorine. About 600 cc. of a 50% solution of commercial potassium bromide were placed in a one-liter distilling flask with a ground stopper, and in the solution was dissolved somewhat over 400 g. of bromine. The side tube of the flask was inserted for some distance in one end of a glass condenser, while the other end of the condenser tube delivered into a Jena flask cooled with ice. With this apparatus the bromine could be distilled from the solution with minimum loss. Three portions of bromine were distilled from the same potassium bromide solution.

Next, one-fourth of the product was converted into potassium bromide by addition to recrystallized potassium oxalate, and the remaining three-fourths of the bromine was distilled from solution in this potassium bromide in the fashion described above. This second distillation, from a bromide which already must have been nearly free from chloride, has in the past been found amply sufficient to remove chlorine. Nevertheless, as will be described, the bromine later received still a third distillation from even purer potassium bromide.

In order to remove organic matter, the bromine was next changed to potassium bromide and fused. All of the twice-distilled bromine was converted into potassium bromide by addition to aqueous potassium oxalate, which had been recrystallized until free from chloride, and the solution was freed from iodine by boiling, with occasional addition of small amounts of the pure bromine. Then the solution was evaporated to dryness, and the salt was fused in a platinum dish. During the fusion a small amount of recrystallized potassium permanganate was added in order completely to oxidize organic matter. Material which had been fused with permanganate had no perceptible odor even while warm, whereas, if the addition of the permanganate was omitted, the salt had a distinct "organic" odor. The treatment with permanganate also must have eliminated any residual iodine. The purification of much of the

¹ THIS JOURNAL, 36, 1088 (1914); *Z. anorg. Chem.*, 87, 353 (1914).

² *Proc. Amer. Acad.*, 47, 585 (1912); THIS JOURNAL, 34, 1644 (1912).

bromine, up to this point, was performed by Mr. M. R. Grose. From this potassium bromide, bromine was prepared as needed by dissolving in water and adding twice-recrystallized potassium permanganate and sulfuric acid which had been heated to fuming with a small amount of permanganate. Only about four-fifths of the bromine was freed from the bromide, so that the product thus received still a third distillation from a very pure bromide. The bromine was always employed in the form of hydrobromic acid.

Hydrobromic Acid.—Hydrobromic acid was used either in the gaseous form, or in solution. It was always synthesized from the purified bromine and pure hydrogen, since this method seemed to offer fewest possibilities for contamination during the process of manufacture. Pure hydrogen was generated electrolytically in a series of cells, each of which consisted of zinc amalgam—hydrochloric acid—platinized platinum¹ (see figure). Hydrogen gas prepared in this way is free from arsine and hydrocarbons.² It contains, of course, hydrochloric acid and water vapor, but these were easily removed by passing the gas through tubes containing fused potassium hydroxide. The gas was charged with bromine in a small bulb, and then was conducted over either platinized asbestos or platinized pumice in a hard glass tube heated to dull redness. The pumice seemed to retain its catalytic power longer than the asbestos. In order to produce the maximum yield, the bromine was kept at about 44° by means of a water bath, since at that temperature the vapor pressure of bromine is about one-half atmosphere. Usually a very slight excess of hydrogen was maintained, so that the resulting gas mixture was nearly, if not quite free from bromine. To prepare hydrobromic acid solution, the gas was conducted into water until acid of nearly constant-boiling composition was obtained. Then the solution was subjected to three distillations through a quartz condenser, the first runnings being discarded in each distillation.

Silver.—Silver was prepared by methods which have frequently been used in the Harvard Laboratories for the purpose. Since the purification of silver has been many times described in some detail, it is necessary only to outline the processes employed. Crude metallic silver was dissolved in nitric acid, and the chloride was precipitated in strongly acid solution with an excess of hydrochloric acid. The precipitate was thoroughly washed, dissolved in concentrated ammonia, and reprecipitated with an excess of nitric acid. Reduction of the chloride by means of sodium hydroxide and sugar followed, and the product, after thorough washing, was fused on charcoal before a blowpipe. The buttons of metal were cleaned by scouring and etching. Then they were dissolved in redistilled nitric acid,

¹ Cooke and Richards, *Proc. Amer. Acad.*, 23, 149 (1887).

² See also Baxter and Hoover, *THIS JOURNAL*, 34, 1657 (1912).

and the metal was again precipitated from neutral solution with ammonium formate, which had been made from redistilled materials. Prolonged washing was necessary before the wash waters were free from ammonia. The product was dried and again fused before a clean blast lamp, in a porcelain crucible lined with very pure lime. This lime was made from calcium oxide and nitrate, both of which had been very carefully freed from foreign metals by crystallization of the nitrate. After being etched with nitric acid, the buttons were purified electrolytically in a cell in which a piece of the purest silver served as cathode, one or more of the buttons as anode, and a nearly neutral solution of one of the buttons as electrolyte. The washed electrolytic crystals were finally fused upon lime boats in a current of pure hydrogen. In order completely to remove adhering lime, the buttons were etched with dilute nitric acid, thoroughly washed with dilute ammonia and water, and then dried by heating in a vacuum to about 400° in a hard glass tube. This specimen of silver is designated Sample I. In many of the experiments, specimens of silver prepared in an identical fashion for other investigations were employed. Sample II was purified by Mr. W. H. Whitcomb,¹ Sample III by Mr. A. C. Boylston,² and Sample IV by Dr. H. C. Chapin.³ Sample I was used in Analyses 6, 7, 9, 10, 11, 12, 16, 32, 34, 35, 36, 37, 38, 39, 40, 42, 44, 45, and 47; Sample II in Analyses 5, 8, 14, 15, 19, and 33; Sample III in Analyses 17, 41, 46, and 48; and Sample IV in Analyses 18 and 43. In Analyses 1, 2, 3, 4, and 13 it is uncertain whether Sample I or II was employed. So far as could be determined by the results of the analyses these four samples of silver were exactly alike. This matter is further considered on page 1058.

Purification of Lead Nitrate.

Since the lead bromide was always made by precipitation from a nitrate solution, the preparation of pure lead nitrate was one of the most important operations. Several methods were used for the purification of the salt: first, electrolysis with a dissolving anode; second, simple recrystallization of the nitrate; and third, precipitation of sulfate or chloride. In fact the second method was used also in conjunction with the first and third.

For the electrolytic purification a cell was used consisting of an anode of crude sheet lead, a platinum cathode, and, as electrolyte, a nearly saturated slightly acid solution of lead nitrate. The crystals of metallic lead which formed on the cathode during electrolysis were frequently removed by means of a glass rake, washed thoroughly, and centrifugally

¹ For an investigation upon the atomic weight of neodymium, not yet published.

² Baxter, Moore and Boylston, *Proc. Amer. Acad.*, 47, 585 (1913); *THIS JOURNAL*, 34, 1644 (1912).

³ Baxter and Chapin, *Proc. Amer. Acad.*, 46, 213 (1910); *THIS JOURNAL*, 33, 116 (1911).

drained in porcelain Gooch crucibles. The crystals rusted rapidly, *hence they were subsequently reduced by fusion in a current of illuminating gas.* Unglazed porcelain boats were filled with the crystals, and placed in an electrically heated porcelain tube. The illuminating gas was scrubbed with wet glass wool, and partially purified and dried by concentrated sulfuric acid and fused sodium hydroxide. Since the metal adhered strongly to the porcelain, the boat was then heated in the air, and the metal poured into a wooden mould.

The progress of the purification of this material was followed by photographing the ultraviolet spectrum of the lead spark by means of a Féry quartz spectrograph. In order to produce electrodes, the lead was melted in a hard glass tube or porcelain crucible, and drawn up into glass capillary tubes. The original sheet lead was found to contain a small amount of copper and a trace of silver. After the first electrolysis the copper and silver lines appeared in the spectrum in almost undiminished intensity. A second electrolysis followed. In this case the cathode was a small piece of the once electrolyzed lead, and the anode larger pieces of the same material. The electrolyte was made from the once purified lead by solution in nitric acid and crystallization of the nitrate. Since the greater part of the copper was contained in the mother liquor, the crystals were dissolved to form the electrolyte. During this second electrolysis, but not during the first, the anode was enclosed in a clean cotton bag to prevent the anode slime from contaminating the crystal deposit. The product of the second electrolysis was washed, dried and fused, as described above. Spectrographic examination of the twice electrolyzed material showed that copper and silver were still contained in the metal, although the proportions of these impurities may have diminished slightly.

With the hope that the transfer of silver and copper from anode to cathode would proceed less readily with a chloride electrolyte, a portion of the once electrolyzed material was subjected to a second electrolysis through a hot saturated solution of lead chloride containing a small amount of hydrochloric acid. The electrolytic crystals were somewhat larger than those obtained from the cold nitrate process. They were washed and dried as before, and spark electrodes were made from a portion of the product. While silver and copper lines were still plainly visible in the spectrum, the diminution in the proportions of these metals was greater than in the nitrate electrolysis. Since, however, the electrolytic purification seemed, on the whole, unsatisfactory, no further attempts were made to purify the material in this way.

None of this electrolyzed material was used directly for the preparation of lead bromide, but it was first subjected to crystallization as nitrate. About 170 g. of lead which had been twice electrolyzed from nitrate were dissolved in nitric acid, which had been distilled in quartz, and the excess

of acid was removed by evaporating almost to dryness. The residue was dissolved in water and evaporated in a platinum dish on an electric stove nearly to the saturation point. Instead of allowing the salt to crystallize by cooling, it was precipitated by adding a large quantity of redistilled nitric acid to the hot solution, which was then allowed to cool. The relatively pure crystals were centrifugally drained in platinum Gooch crucibles, and were washed with several portions of concentrated nitric acid. The salt was then recrystallized twice more in the same way. In order to determine whether purification was effected in this process, metallic lead was made from a portion of the nitrate by electrolysis upon a platinum cathode, and the electrolytic crystals were washed and converted into spark electrodes. In the ultraviolet spectrum of this metal no copper or silver lines could be seen, nor were there any other lines visible which were not observed in all of the lead samples which we prepared. This sample of lead nitrate is designated Sample A.

Sample B of lead nitrate was made in exactly the same way from metal which had been electrolyzed once through the nitrate, once through the chloride. In order to obtain some evidence as to the proportions of impurities in the original lead, the mother liquors from the three crystallizations of the nitrate of Sample A were freed from the greater part of the lead by evaporating with an excess of sulfuric acid, diluting, and adding alcohol. To the filtrate from the lead sulfate, ammonia was added in excess, and the very slight precipitate, apparently iron in large part, was removed by filtration. The filtrate was evaporated to small bulk, and after precipitation with an excess of potassium hydroxide, the copper and silver oxides were collected on a filter paper, ignited, and weighed. From the original 170 g. of lead nitrate, 0.0088 g. of copper oxide and silver were obtained, which indicates a percentage of silver and copper together of only 0.004. The electrolytic metal from which Sample B was made was found in the same way to contain less than 0.003% of silver and copper.

Another sample of lead nitrate was purified simply by repeated crystallization. About one kilogram of commercial salt was dissolved in water and the solution was filtered through a platinum-sponge Gooch crucible. Then the solution was evaporated, and the salt was crystallized four times in Jena vessels with addition of a large excess of redistilled nitric acid, as previously described. After the fourth crystallization, the material was transferred to platinum vessels, and recrystallized three times more, with a second filtration through platinum-sponge between the sixth and seventh crystallizations. All the nitric acid was distilled in quartz, and the crystals were centrifugally drained and rinsed with nitric acid. This material is designated Sample C.

Sample D of lead nitrate was purified first by Dr. J. W. Shipley, by precipitating lead chloride from a solution of the commercial nitrate,

converting the thoroughly washed lead chloride into sulfide by suspending the chloride in water and saturating with well scrubbed hydrogen sulfide gas, and finally dissolving the sulfide in nitric acid. The nitrate was crystallized once in glass, and then was subjected to three additional crystallizations in platinum. The solution of the nitrate was filtered through platinum sponge after the first crystallization.

The ultraviolet spark spectra of Samples C and D were found to be identical with those of Samples A and B. The geographical origin of these samples of lead is unknown to us, but it is highly probable that the sheet metal, at any rate, is of American origin, although the nitrate may have been either American or European material. This question of origin will be discussed more fully in a later portion of this paper (page 1048).

Preparation of Lead Bromide.

To prepare lead bromide, pure lead nitrate was dissolved in water in a quartz dish, and a slight excess of the purest hydrobromic acid solution was added. The precipitated bromide was collected on platinum Gooch crucibles without mat of any sort, before any free bromine appeared in the mother liquors, and was centrifugally drained and washed. On account of the low solubility of lead bromide, crystallization of the product from water was avoided by the device described in the preceding paper, of dissolving the lead bromide in hot constant-boiling hydrobromic acid in a quartz dish, and reprecipitating the salt by the addition of water and cooling. During the solution of the lead bromide in hydrobromic acid for the first time, bromine was set free, presumably by traces of included nitric acid. Therefore, before draining the crystals in platinum, they were thoroughly washed by decantation with ice-cold water. All of the lead bromide analyzed was recrystallized in this way at least three times, and Sample CD, which was a mixture of Samples C and D, was further crystallized three times more, that is, six times in all. The purified material was preserved in platinum over fused potassium hydroxide in a desiccator. Since lead bromide darkens in the light,¹ the salt was protected from light so far as possible. The various preparations of lead bromide are designated by the letter corresponding to the nitrate samples from which they were made.

Drying of Lead Bromide for Analysis.

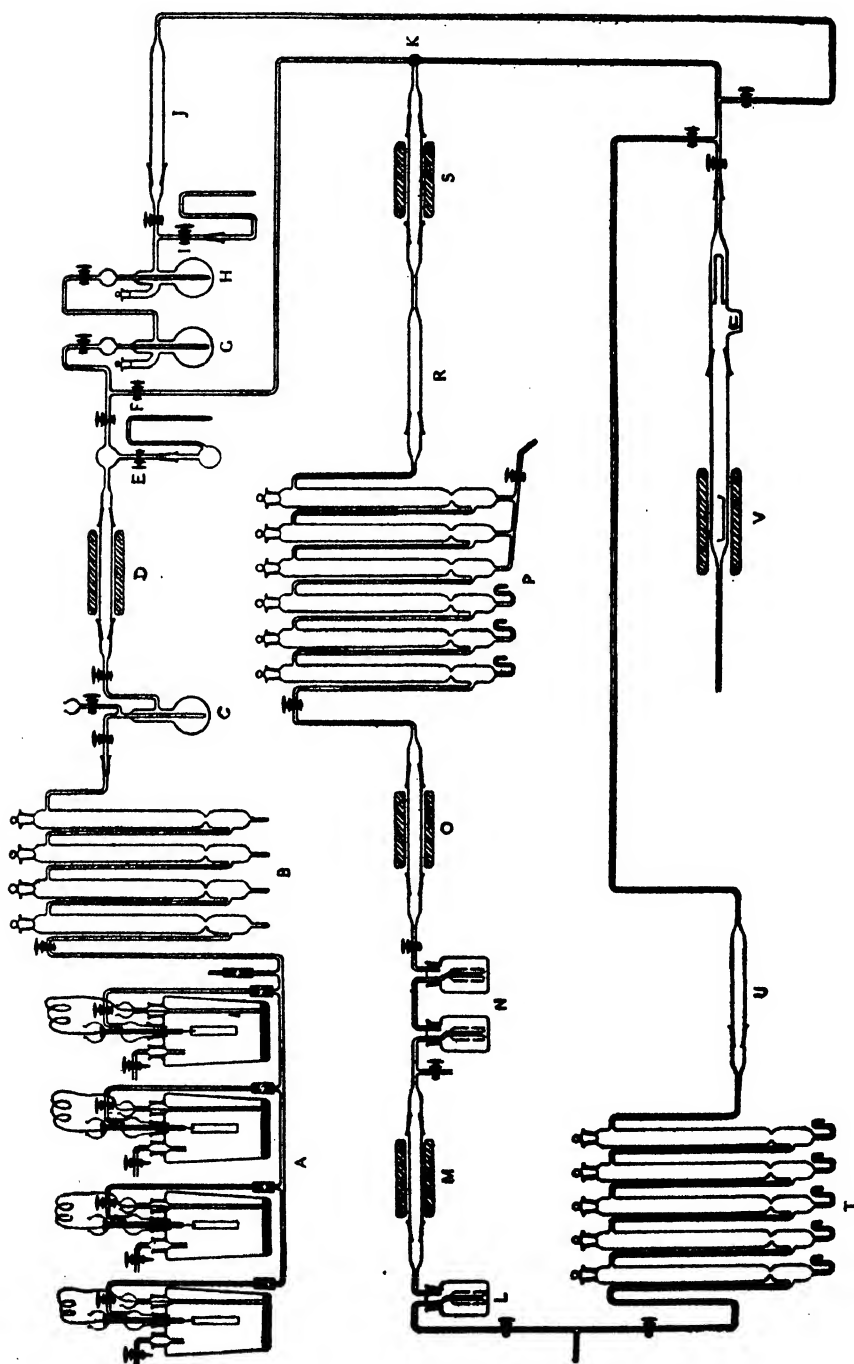
The lead bromide was prepared for analysis by fusion in an atmosphere charged with hydrobromic acid gas, after the salt had been dried as far as possible in a vacuum desiccator over fused potassium hydroxide. Lead bromide which has been fused in this way, when treated with water yields a considerable amount of insoluble basic salt. Evidence that the salt which has been fused in hydrobromic acid is initially neutral,

¹ Norris, *Ann. Chem.*, 117, 189 (1861).

and that the basic salt is formed by hydrolysis during solution has already been presented in the preceding paper, and in our work with lead bromide no new evidence contradictory to this point of view was obtained. In fact, in two experiments (Analyses 5 and 11) where the lead bromide was initially very moist when the drying commenced and hydrolysis therefore was to be expected if it occurs at all during the drying, the fused material proved identical in composition with the other specimens. The difficulty was avoided in the analytical work by dissolving the salt in water which had been made slightly acid with nitric acid. Even under these conditions no evidence could be obtained of loss of either hydrobromic acid by evaporation, or of bromine by oxidation. As in the previous research, the agreement of the analyses of different preparations is valuable confirmation of the claim that the fused material was strictly neutral.

Another possibility which we considered was that of dissociation of the salt into either metal or sub-bromide with loss of bromine. A decomposition apparently occurs when lead bromide is exposed to light, although heating or even fusion in a neutral atmosphere gives no evidence of dissociation. The point was tested, however, by experiments in which the lead bromide was fused in hydrobromic acid containing free bromine, as well as in hydrobromic acid containing considerable hydrogen. So far as the appearance of the preparations and the results of the analyses are concerned, absolutely no difference could be detected.

The apparatus for fusing in hydrobromic acid gas was modified considerably from that used previously, enough so that it seems worth while to show a detailed diagram of the apparatus (see figure). Hydrogen was evolved by means of electrolytic generators, A, each consisting of the cell zinc amalgam—hydrochloric acid—platinized platinum (see page 1030). These generators were constructed entirely of glass. The gas was purified and dried by passing through several tubes containing fused potassium hydroxide B, and was then partly saturated with the purest bromine in a flask C, which was kept at a temperature of 44° or below. The hydrogen and bromine were combined in a hard glass tube D, containing either platinized asbestos or platinized pumice, heated electrically to dull redness, and the resulting hydrobromic acid was collected in constant-boiling hydrobromic acid solution in the flasks G and H, until the solutions in the two flasks were saturated at room temperature. As the saturation point was approached, the hydrobromic acid gas which escaped from the flask unabsorbed, was collected by being conducted into water through the outlet I. The small amount of bromine, which occasionally accompanied the hydrobromic acid, and which was dissolved in the fuming solution, was eliminated by introducing a small amount of very pure iron into the flasks G and H through the side arms. The resulting solution of ferrous bromide retains very effectively every trace of free bromine,



and is far more effective than a tube of dry ferrous bromide. The iron used for the purpose was free from every impurity except possibly platinum. It was obtained by reduction of the purest ferric oxide by Baxter and Hoover¹ in a determination of the atomic weight of iron in this way. Nitrogen was charged with hydrobromic acid gas by passing through the fuming solution, through the stop-cock F, and the gas mixture was dried by means of fused calcium bromide in the tube J, before being led into the fusion apparatus V. While fused calcium bromide is not a perfect drying agent, Baxter and Warren² have found that a liter of gas passed over this substance at 25° retains only 0.0002 g. of moisture. A current of hydrogen charged with hydrobromic acid could be produced by passing hydrogen through the cold bromine, then over hot platinum, and finally through the fuming hydrobromic acid solution and the calcium bromide tube, while a current of hydrobromic acid and bromine was obtained by warming the bromine flask considerably above 44°, at which temperature the bromine has a vapor pressure of one-half atmosphere, then through the catalysis tube, and through a drying tube containing calcium bromide. This latter arrangement, which was used only a few times, is not shown in the diagram.

Nitrogen was made by the Wanklyn process, by charging air with ammonia in a gas washing bottle, I, filled with concentrated ammonia solution (sp. gr. less than 0.92). In order to reduce the oxygen, the gas mixture was passed through an electrically heated tube, M, filled with copper gauze, and the excess of ammonia was absorbed in dilute sulfuric acid in the two gas washing bottles N. The hydrogen formed by dissociation of the excess of ammonia was oxidized in the tube O, containing hot copper oxide. The nitrogen was now purified and dried in the six towers P. The first one contained beads wet with a concentrated solution of potassium hydroxide. The other five contained concentrated sulfuric acid, which had previously been heated to fuming with a very small amount of potassium dichromate. Residual moisture was absorbed in a tube, R, containing phosphorus pentoxide which had been resublimed in a current of oxygen. Finally, last traces of oxygen were absorbed by hot copper in the hard glass tube S.

Air was purified and dried in the towers T, two of which contained beads wet with silver nitrate solution, one, fused potassium hydroxide, and two, concentrated sulfuric acid, and in the phosphorus pentoxide tube U.

The hydrogen, nitrogen, hydrobromic acid, and air apparatus was constructed entirely of glass. Joints were either fused or ground, the necessary flexibility for detaching the different parts being afforded by numerous glass grids. The ground joints and stopcocks through which the bromine

¹ THIS JOURNAL, 34, 1657 (1912).

² *Ibid.*, 32, 342 (1910).

or hydrobromic acid passed were kept clean and dry, but many of those used for nitrogen, air, and hydrogen were lubricated with a small amount of soft paraffin.

When the lead bromide was fused in either nitrogen or hydrogen charged with hydrobromic acid, either a platinum or a quartz boat was used, but when the fusion atmosphere contained bromine, of course a quartz boat was employed. The boat containing the partially dried lead bromide was placed in a quartz tube which formed part of the usual form of "bottling apparatus"¹ (V in figure). After the air had been swept out with a slow current of pure nitrogen, and this in turn by the fusion atmosphere containing hydrobromic acid, the salt was gently heated with an electric coil or with an aluminum block furnace, in order to drive off as much as possible of the residual moisture before fusion. The temperature was then raised by means of a "Ni-chrome" sleeve, until the salt was fused. As soon as the salt had solidified, the fusion atmosphere was displaced with pure nitrogen, and this finally with pure dry air, and the boat and contents were transferred to the weighing bottle, in which they were to be weighed, without exposure to the outside air. While the hydrobromic acid was being displaced by nitrogen and air, a portion of the gas was sent back through the tube I, in order to prevent possible contamination of the atmosphere of the bottling apparatus with hydrobromic acid while the boat was being transferred to the weighing bottle. The weighing bottle with its contents was then placed in a desiccator, and left near the balance for some time before being weighed. Neither the platinum nor the quartz boat was appreciably attacked in these experiments.

Analysis of the Lead Bromide.

The fused and weighed lead bromide was dissolved and first compared with a weighed, very nearly equivalent, quantity of the purest silver, then the precipitated bromide was collected, dried, and weighed. This process is identical with the one which has been found very successful, both in the Harvard and in other laboratories. Very few deviations from the ordinary method of procedure were made. This method gives a comparison of the atomic weight of lead with those of silver and bromine, but any subsequent change in the standard of comparison, silver, will necessitate a change in the same proportion in that of lead.

Although lead bromide is not so soluble in water as lead chloride, yet a liter of water at ordinary temperatures will dissolve about 9 g. of salt. Solution of the fused material, however, takes place slowly, and we found it highly desirable to conduct the solution in nearly boiling water, as has been explained in the previous paper. When neutral lead bromide is dissolved in water, the salt is partially hydrolyzed, with precipitation of a basic bromide. In the earlier work by Baxter and Thorvaldson,

¹ Richards and Parker, *Proc. Amer. Acad.*, 32, 59 (1896).

this hydrolysis was prevented by adding a considerable amount of acetic acid. Since, however, lead acetate is a slightly dissociated substance, we were somewhat concerned for fear this salt might be occluded by the silver bromide, and therefore we decided to substitute for acetic acid a quantity of a strong acid of equivalent acidity. At first, an exactly known amount of hydrobromic acid was used, but very shortly we discovered that a small amount of even nitric acid could be employed without the loss of a perceptible amount of either hydrobromic acid or bromine. The latter point was tested very carefully by distilling solutions of lead bromide containing nitric acid, collecting the distillate in alkali, and after evaporation, testing the solution for bromide.

In one experiment about 4 g. of lead bromide were dissolved in a liter of water, and 0.2 cc. of concentrated nitric acid was added. The solution was boiled in a Jena flask, fitted to a quartz condenser, and the distillate was collected in dilute ammonia. After 300 cc. of distillate had passed over, the ammoniacal solution was evaporated upon an electric stove to a volume of about 10 cc., and the solution was tested for bromide by adding a small amount of silver nitrate. Comparison with a standard solution of bromide in a nephelometer showed only 0.01 mg. of bromide in the solution. A repetition of the experiment, using 5 g. of lead bromide and 2.0 cc. of concentrated nitric acid, yielded a distillate containing 0.03 mg. During the solution of lead bromide for analysis the conditions were far less favorable for the liberation of hydrobromic acid and bromine, because, in the first place, much less nitric acid was found necessary to prevent formation of basic salt, and in the second place, while the solution occasionally was heated barely to boiling, very little vapor actually escaped from the solution flask. Additional experiments were made in order to find out how much nitric acid really was necessary in order to liberate an appreciable amount of bromine. For this purpose, the above experiments were repeated, using gradually increasing amounts of nitric acid. To a solution of 4 g. of lead bromide in 1200 cc. of water, nitric acid was added in successive portions, and the solution was distilled into a solution of halogen-free sodium carbonate. Each portion of distillate consisted of 25 cc., and before the succeeding distillation was carried out, the liquid distilled was replaced by an equal amount of water. The separate distillates were acidified with nitric acid, and after silver nitrate solution had been added, nephelometric comparisons were made with solutions of known bromide content.

| | | | | | |
|------------------------------|-------|-------|-------|-------|-------|
| Nitric acid added (cc.)..... | 0.10 | 0.60 | 2.10 | 4.65 | 9.65 |
| Bromide found (mg.)..... | 0.000 | 0.000 | 0.005 | 0.015 | 0.150 |

These figures show conclusively that error from evaporation of either hydrobromic acid or bromine could not possibly have taken place during the solution of the lead bromide for analysis.

The method of carrying out the solution was as follows: The boat containing the weighed sample of lead bromide was transferred to a two-liter Jena glass Erlenmeyer flask, containing about one liter of the purest water. The weighing bottle was rinsed with hot water and the rinsings added to the flask. A column of seven bulbs, ground into the neck of the flask, was inserted to catch any possible spray if the solution happened to boil, and to serve as a reflux condenser. Finally two drops (0.10 cc.) of redistilled nitric acid were added. The flask and its contents were then heated over an electric stove, until solution was complete. This required several hours. In fact, the solution was generally heated over night.

Even after the lead bromide was dissolved, there still remained, usually floating on the surface of the solution, a small amount of black material. Preliminary investigation, both by Dr. Thorvaldson and ourselves, showed that the residue contained neither platinum nor lead. Furthermore, the platinum boat itself remained practically constant in weight. In a few preliminary experiments, this residue was neglected, but in most of the experiments, the weight of the black residue was determined by filtration upon a weighed platinum-sponge Gooch crucible. Similar material was found by Baxter and Thorvaldson, as described in the previous paper, and the nature of the residue has been discussed in a recent paper by Baxter and Hartmann,¹ where evidence is presented which shows it to consist of carbon and silica. In the course of our experiments we were able to make a quantitative analysis of a portion of material. The Gooch crucible containing the residue from several analyses was gently ignited. The black appearance of the residue disappeared with obvious combustion (sparks), confirming the conclusion that a portion of the residue is carbon. A white residue, presumably of silica, could still be seen. This was carefully removed by gently rubbing with a clean finger, and the crucible was carefully dried and reweighed.

| | |
|--|----------|
| Original weight of crucible..... | 24.05098 |
| Weight of crucible + residue..... | 24.05200 |
| Weight of residue..... | 0.00102 |
| Weight of crucible after ignition..... | 24.05167 |
| Weight of carbon..... | 0.00035 |
| Weight of cleaned crucible..... | 24.05100 |
| Weight of silica..... | 0.00067 |

It is interesting to see that about one-third of the residue was carbon, and two-thirds silica. The carbon undoubtedly originated largely in dust and lint from the room, but possibly in part in residual organic matter in the reagents in spite of the pains taken to prevent the difficulty. It seems likely that the silica resulted from attacking of the quartz dish in which the lead bromide was recrystallized. Whatever the origin of

¹ THIS JOURNAL, 37, 113 (1915).

the residue, it could have had little effect upon the final result, because the weight was determined in each separate experiment, and because the proportion of residue was very small. In thirty-six experiments with lead bromide and chloride, we found on an average only 0.004% of residue. The method of determining the residue in each separate experiment seemed far preferable to applying an average correction to the results, because the percentage varied from almost nothing to nearly 0.01% in a few experiments. In Analyses 1 and 2 there was no visible residue, and no filtration was therefore carried out. These two analyses, nevertheless, gave results essentially identical with those in which the residue was considerable. Since the silver bromide has very nearly the same weight as the lead bromide from which it is obtained, and since the black residue, if not determined, would be collected and weighed with the silver bromide, neglecting the residue would affect the comparisons with silver only, which would then yield results a little more than 0.01 unit too high for the atomic weight of lead.

In filtering the solution of lead bromide, the thistle-tube holding the weighed platinum-sponge crucible was inserted in the upper tubulature of a large bell-jar, and the solution was caught in a three-liter precipitating flask. The solution came in contact only with glass, and was caught in such a way that spattering could not possibly have taken place. After the filtration of the solution, the platinum mat was very thoroughly washed with a large volume of warm water, and the crucible was dried over an electric stove at about 250° for half an hour. It was easily shown that the carbon residue did not oxidize during the drying, by reheating the crucible over a long period and reweighing. Furthermore, the platinum mat remained undissolved by the slightly acid solution of lead bromide. One crucible showed a gain in weight after cleaning of 0.00007 g. during six filtrations, and another a gain of 0.00002 g. during five filtrations.

Before precipitation, the solution of lead bromide was diluted until less than 0.02 *N*. Usually this concentration was reached during the washing of the crucible. When the corrected weight of the lead bromide had been found, a quantity of pure silver, very nearly equivalent to the lead bromide, was carefully weighed out. This silver consisted almost entirely of one or two large buttons, but the final adjustment of the weight was secured with tiny electrolytic crystals which had been heated to 500° in a vacuum. The silver was dissolved in a flask provided with a column of bulbs to prevent loss by spattering, but effervescence during solution was prevented by using a fairly concentrated solution of nitric acid, and by heating very gently. As soon as the metal had disappeared, the solution was diluted to about 200 cc., and heated until the nitrous acid formed during the solution of the silver had been destroyed. Then

the solution was further diluted in the dissolving flask until the concentration was no higher than 0.03 *N*.

In precipitating the silver bromide, generally, because of convenience, the silver solution was added to the bromide solution, although in a few instances the reverse method was employed, in order that if occlusion of either bromide or silver occurred it might be detected. That slight occlusion was likely to take place was obvious from the fact that during the early precipitations, where the concentrations of the solutions were somewhat higher than those given above, material apparently was extracted from the precipitate by long standing. For this reason, too, especial pains were taken during precipitation to agitate the mixed solutions thoroughly.

The silver nitrate solution was added to the bromide solution slowly with continual gentle agitation. At the end of the precipitation the flask was closed with its glass stopper, and gently shaken for a very short time. Then it was allowed to stand with occasional shaking for a week, before the supernatant liquid was tested in a nephelometer for excess of bromide or silver. Portions of 25 cc. of the clear liquid were transferred to test tubes, and treated, in one case, with a cubic centimeter of 0.01 *N* bromide; in the other, with the same amount of 0.01 *N* silver nitrate. After thorough stirring, they were occasionally examined in the nephelometer until the ratio of the opalescence in the two tubes became constant. If an excess of either bromide or silver was found, and this was usually the case, the deficiency was made up by adding 0.01 *N* solutions to the main solution in the flask, and the solution was shaken and again allowed to stand before being tested. The process was continued until the solution contained equivalent amounts of bromide and silver. At this point, owing to the slight solubility of silver bromide, the test portions remained very nearly clear after the addition of the bromide and silver solutions. In a few analyses the end point seemed to change very slightly with time, indicating that occluded or entangled matter was being slowly leached from the precipitate. This change in the end point was at the worst only a matter of a few tenths of a mg., and came to an end within two or three weeks. In all the analyses testing was continued until we were sure that no further change was occurring.

As stated above, in three analyses, Nos. 10, 11, and 13, the bromide solution was poured into the silver nitrate solution. The results of these analyses were no different from the results of those precipitated in the reverse fashion.

The precipitation of the silver bromide was made in a room illuminated only with red light, and during the subsequent manipulations even diffused white light was never allowed to fall upon the precipitate for more than an instant.

As soon as the exact end point had been determined, 0.02 g. of dissolved silver nitrate were added for each liter of solution, and after standing for a short time, the supernatant liquid was poured through a large weighed platinum-sponge Gooch crucible. The precipitate was washed ten times by decantation with a solution containing 0.01 g. of silver nitrate per liter, and once or twice with chilled water, and was transferred quantitatively to the crucible with ice-cold water. The crucible and contents were dried at 160° for about 15 hours in a well ventilated electric oven, and then, after being allowed to reach the temperature of the balance room in a desiccator, were weighed. The main mass of precipitate was transferred to a small porcelain crucible, which was weighed with its cover, and then, after being heated above the fusing point of the silver bromide, was weighed again. The loss in weight was assumed to represent moisture retained by the silver bromide. In accordance with the results of previous similar experiments by others, the silver bromide was never found to contain more than 0.006% of residual moisture, the average proportion being 0.003%. The filtrate and the silver nitrate wash water were assumed to contain no dissolved silver bromide, since the solubility of silver bromide, even in pure water, is only 0.1 mg. per liter at room temperature. Furthermore, since the pure water used in the rinsing and transference of the precipitate was previously chilled, the amount of silver bromide thus lost must have been very small indeed, judging from the diminution in the solubility of silver chloride with the temperature. Since the volume of the aqueous washings was only a few hundred cc., no correction is applied for dissolved silver bromide.

The precipitating flask was rinsed with a small amount of distilled ammonia. These rinsings were diluted to 250 cc., and the bromide content was determined in a nephelometer by adding silver nitrate solution, and comparing with standard solutions of bromide. As a rule, about 0.1 mg. was found in this way.

All weighings were made upon a No. 10 Troemner balance, used only for exact work. The atmosphere of the balance case was partially dried by solid potassium hydroxide. In order to dissipate electrostatic charges upon the objects weighed, the balance case also was provided with a small amount of crude radium bromide.

The gold plated weights were standardized to hundredths of a milligram by the Richards¹ method.

All weighings were made by substitution for counterpoises as nearly as possible like the objects weighed in shape, volume, and material, except in the case of the small platinum crucible used in collecting the black residue, which was substituted for weights.

¹ THIS JOURNAL, 22, 144 (1900).

SERIES I.—THE ATOMIC WEIGHT OF LEAD.

PbBr₃ : 2Ag.

Ag = 107.880.

Br = 79.916.

| Number of analysis. | Sample of PbBr ₃ . | Fusion atmosphere. | Wt. of PbBr ₃ in vacuum. Grams. | Wt. of residue. Gram. | Corr. wt. of PbBr ₃ in vacuum. Grams. | Wt. of Ag in vacuum. Grams. | Wt. of Ag added. Gram. | Corr. wt. of Ag in vacuum. Grams. | Ratio PbBr ₃ : 2Ag. | At. wt. of Pb. |
|---------------------|-------------------------------|-----------------------|--|-----------------------|--|-----------------------------|------------------------|-----------------------------------|--------------------------------|----------------|
| 1 | C | HBr + H ₂ | 5.27845 | | 5.27845 ¹ | 3.10275 | -0.00004 | 3.10271 | 1.70124 | 207.23 |
| 2 | C | HBr + H ₂ | 2.65094 | | 2.65094 ¹ | 1.55869 | -0.00047 | 1.55822 | 1.70126 | 207.23 |
| 3 | C | HBr + N ₂ | 4.08449 | 0.00039 | 4.08410 | 2.40152 | -0.00048 | 2.40104 | 1.70097 | 207.17 |
| 4 | D | HBr + N ₂ | 4.97508 | 0.00040 | 4.97468 | 2.92493 | -0.00020 | 2.92473 | 1.70090 | 207.15 |
| 5 | CD | HBr + N ₂ | 4.05573 | 0.00032 | 4.05541 | 2.38423 | -0.00025 | 2.38398 | 1.70111 | 207.20 |
| 6 | CD | HBr + N ₂ | 3.44158 | 0.00019 | 3.44139 | 2.02322 | -0.00036 | 2.02288 | 1.70123 | 207.23 |
| 7 | CD | HBr + N ₂ | 5.17416 | 0.00029 | 5.17387 | 3.04178 | -0.00020 | 3.04158 | 1.70105 | 207.19 |
| 8 | CD | HBr + N ₂ | 3.84522 | 0.00025 | 3.84497 | 2.26058 | -0.00036 | 2.26022 | 1.70115 | 207.21 |
| 9 | CD | HBr + H ₂ | 4.30542 | 0.00029 | 4.30513 | 2.53089 | -0.00003 | 2.53086 | 1.70105 | 207.19 |
| 10 | CD | HBr + H ₂ | 4.53467 | 0.00022 | 4.53445 | 2.66542 | +0.00007 | 2.66549 | 1.70117 | 207.21 |
| 11 | A | HBr + N ₂ | 5.78467 | 0.00030 | 5.78437 | 3.40050 | -0.00006 | 3.40044 | 1.70107 | 207.19 |
| 12 | A | HBr + N ₂ | 4.87104 | 0.00025 | 4.87079 | 2.86350 | -0.00013 | 2.86337 | 1.70107 | 207.19 |
| 13 | A | HBr + N ₂ | 6.28465 | 0.00019 | 6.28446 | 3.69427 | +0.00020 | 3.69447 | 1.70104 | 207.19 |
| 14 | B | HBr + N ₂ | 4.74644 | 0.00005 | 4.74639 | 2.78996 | +0.00015 | 2.79011 | 1.70115 | 207.21 |
| 15 | B | HBr + N ₂ | 6.82444 | 0.00020 | 6.82424 | 4.01203 | -0.00055 | 4.01148 | 1.70118 | 207.21 |
| 16 | B | HBr + N ₂ | 6.53721 | 0.00032 | 6.53689 | 3.84278 | -0.00004 | 3.84274 | 1.70110 | 207.20 |
| 17 | B | HBr + Br ₂ | 4.10128 | 0.00030 | 4.10098 | 2.41073 | +0.00015 | 2.41088 | 1.70103 | 207.18 |
| 18 | B | HBr + Br ₂ | 2.64271 | 0.00015 | 2.64256 | 1.55327 | +0.00025 | 1.55352 | 1.70101 | 207.18 |
| 19 | A | HBr + Br ₂ | 6.30717 | 0.00034 | 6.30683 | 3.70759 | -0.00041 | 3.70718 | 1.70125 | 207.23 |
| Average | | | | | | | | | 1.70111 | 207.20 |

¹ No visible residue. Solution not filtered.

SERIES II.—THE ATOMIC WEIGHT OF LEAD.

PbBr₂ : 2AgBr.

Ag = 107.880.

Br = 79.916.

| Number of analysis. | Sample of PbBr. | Fusion atmosphere. | Wt. of PbBr in vacuum. Grams. | Wt. of residue. Grams. | Corr. wt. of PbBr in vacuum. Grams. | Wt. of AgBr in vacuum. Grams. | Loss on fusion. Grams. | AgBr dissolved from flask. Grams. | Corr. wt. of AgBr in vacuum. Grams. | Ratio PbBr ₂ : 2AgBr. | At. wt. of Pb. |
|---------------------|-----------------|-----------------------|-------------------------------|------------------------|-------------------------------------|-------------------------------|------------------------|-----------------------------------|-------------------------------------|----------------------------------|----------------|
| 20 | CD | HBr + N ₂ | 4.05573 | 0.00032 | 4.05541 | 4.15023 | 0.00016 | 0.00010 | 4.15017 | 0.97717 | 207.18 |
| 21 | CD | HBr + N ₂ | 3.44158 | 0.00019 | 3.44139 | 3.52230 | 0.00015 | 0.00009 | 3.52224 | 0.97705 | 207.14 |
| 22 | CD | HBr + N ₂ | 5.17416 | 0.00029 | 5.17387 | 5.29504 | 0.00011 | 0.00005 | 5.29498 | 0.97713 | 207.17 |
| 23 | CD | HBr + N ₂ | 3.84522 | 0.00025 | 3.84497 | 3.93464 | 0.00025 | 0.00007 | 3.93446 | 0.97726 | 207.22 |
| 24 | CD | HBr + H ₂ | 4.30542 | 0.00029 | 4.30513 | 4.40622 | 0.00014 | 0.00008 | 4.40616 | 0.97707 | 207.15 |
| 25 | CD | HBr + H ₂ | 4.53467 | 0.00022 | 4.53445 | 4.64054 | 0.00013 | 0.00007 | 4.64048 | 0.97715 | 207.18 |
| 26 | A | HBr + N ₂ | 5.78467 | 0.00030 | 5.78437 | 5.91986 | 0.00020 | 0.00010 | 5.91976 | 0.97713 | 207.17 |
| 27 | A | HBr + N ₂ | 4.87104 | 0.00025 | 4.87079 | 4.98473 | 0.00017 | 0.00011 | 4.98467 | 0.97715 | 207.18 |
| 28 | A | HBr + N ₂ | 6.28465 | 0.00019 | 6.28446 | 6.43137 | 0.00023 | 0.00010 | 6.43124 | 0.97718 | 207.19 |
| 29 | B | HBr + N ₂ | 4.74644 | 0.00005 | 4.74639 | 4.85720 | 0.00019 | 0.00007 | 4.85708 | 0.97721 | 207.20 |
| 30 | B | HBr + N ₂ | 6.82444 | 0.00020 | 6.82424 | 6.98385 | 0.00014 | 0.00009 | 6.98380 | 0.97715 | 207.18 |
| 31 | B | HBr + Br ₂ | 4.10128 | 0.00030 | 4.10098 | 4.19799 | 0.00018 | 0.00010 | 4.19791 | (0.97691) (207.09) | |

Average, omitting Analysis 31,

Average of Series I and II,

0.97715 207.18
0.97715 207.19

The following vacuum corrections are applied:

| | Specific gravity. | Vacuum correction per gram. |
|-------------------------|--------------------|-----------------------------|
| Weights..... | 8.3 | |
| Ag..... | 10.49 ¹ | —0.000031 |
| AgBr..... | 6.473 ² | +0.000041 |
| PbBr ₂ | 6.659 ³ | +0.000036 |

Results and Discussion.

Before the results recorded in the preceding table were obtained a preliminary series of determinations was carried out. In these analyses no attempt was made to collect and determine the black residue. Furthermore, several were subject to other uncertainties. The results varied from 207.08 to 207.22, with an average of 207.16. Since these determinations were comparable with those made by Dr. Thorvaldson, whose results are recorded in the preceding paper, it seems unnecessary to give further details. After the procedure had been mastered and various sources of error had been discovered and eliminated, the foregoing "final" series was carried out with the purest materials. All analyses which reached the stage of precipitation are recorded.

The agreement of the various determinations in each series is very satisfactory, when the high atomic weight of lead is taken into consideration. In the comparisons with silver the extreme values differ by 0.08 unit, corresponding to 0.0006 g. of silver for a five gram portion of lead bromide, but except for Analyses 3 and 4, the difference is 0.05 unit, corresponding to 0.0004 g. of silver. In the determination of the silver bromide the agreement is almost as good. Analysis 31 diverges widely from all the others in the series, but, since in this experiment contamination of the silver bromide with glass chips was suspected, the result of this experiment is omitted in computing the average.

In comparing the two series, it can be seen that the titrations against silver give a slightly higher result than the experiments where the silver bromide was weighed. This indicates that for a given amount of silver used, too much silver bromide was obtained, as the following table shows:

| Analyses. | Ag : AgBr. | Analyses. | Ag : AgBr. |
|-----------|------------|------------------|------------|
| 5 and 20 | 0.57443 | 12 and 27 | 0.57444 |
| 6 and 21 | (0.57432) | 13 and 28 | 0.57446 |
| 7 and 22 | 0.57443 | 14 and 29 | 0.57443 |
| 8 and 23 | 0.57447 | 15 and 30 | 0.57440 |
| 9 and 24 | 0.57439 | 17 and 31 | (0.57431) |
| 10 and 25 | 0.57440 | | |
| 11 and 26 | 0.57442 | | |
| | | Average, 0.57443 | |

¹ Richards and Wells, *Pub. Car. Inst.*, 28, 11 (1905); *THIS JOURNAL*, 27, 466.

² Baxter and Hines, *Am. Chem. Jour.*, 31, 224 (1904).

³ Determined in this laboratory by Mr. C. F. Hawkins. Not yet published.

Baxter¹ has already found the probable value of the ratio Ag : AgBr to be 0.57445.

This apparent excess in weight of the silver bromide may have been due either to occlusions by the precipitated silver bromide or to contamination from the ground stoppers of the precipitating flasks, which necessarily were opened several times. The former explanation is less probable, for several of the silver bromide precipitates were very carefully tested for lead with negative results, by solution and reprecipitation, and examination of the mother liquor. With regard to the latter difficulty, every precaution was taken to avoid grinding during the insertion and removal of the stopper, and before using the flask the ground surfaces were made as smooth as possible by wet grinding. In any case the uncertainty in the average of Series I and II is no greater than 0.01 unit.

It is also interesting to compare the results obtained with different specimens of lead bromide, as well as the effect of varying the fusion atmosphere.

| Sample of PbBr ₂ . | PbBr ₂ : 2Ag. | PbBr ₂ : 2AgBr. | Average. |
|-------------------------------|--------------------------|----------------------------|-----------------------|
| A..... | 207.20 | 207.18 | 207.19 |
| B..... | 207.20 | 207.19 | 207.20 |
| C..... | 207.21 | | 207.21 |
| D..... | (207.15) | | (207.15) ² |
| CD..... | 207.20 | 207.18 | 207.19 |
| Average..... | 207.20 | 207.18 | 207.19 |
| Fusion atmosphere. | PbBr ₂ : 2Ag. | PbBr ₂ : 2AgBr. | Average. |
| N ₂ + HBr..... | 207.19 | 207.18 | 207.19 |
| H ₂ + HBr..... | 207.21 | 207.17 | 207.19 |
| Br ₂ + HBr..... | 207.20 | ³ | 207.20 |
| Average..... | 207.20 | 207.18 | 207.19 |

So far as can be told the variations in these results are wholly accidental.

PART II. THE ANALYSIS OF LEAD CHLORIDE.

Because the outcome of the foregoing work as well as of that of Baxter and Thorvaldson indicates a distinctly higher figure for the atomic weight of lead than the value obtained by Baxter and Wilson by the analysis of lead chloride, it became highly important to repeat the work upon lead chloride. At about this time we were informed of the results of Richards and Lambert's analyses of radioactive lead chloride, which indicate a considerably lower value for the radioactive material than for ordinary lead. Thus the question as to whether common lead always possesses the same atomic weight immediately became a vital one. We decided

¹ *Proc. Amer. Acad.*, 42, 201 (1906); *THIS JOURNAL*, 28, 1322 (1906).

² This is the result of one analysis only.

³ In the only analysis in which the silver bromide was collected, contamination of the precipitate was suspected (Analysis 31).

therefore to combine with the investigation of lead chloride the comparison of lead material from different geographical sources. Lead ores were secured from different parts of the United States, from Germany, and from New South Wales, and from these minerals pure material was prepared in essentially the same way in every case. The ores were either nearly pure galena or cerussite in all but one instance. Radioactive minerals in particular were avoided in order to eliminate uncertainty from the possible presence of radioactive lead.

The Purification of Lead Nitrate.

In order to provide a cross connection with the bromide work, one specimen of lead nitrate which had been used in preparing the bromide was also employed as a source of lead chloride. This specimen was Sample D, which had been made from commercial lead nitrate by precipitation of lead chloride and many crystallizations as lead nitrate (see page 1033).

Sample E was prepared from large pieces of clear cerussite from the British Broken Hill Mine, New South Wales, Australia. After solution of the mineral in an excess of nitric acid, an insoluble residue was removed by filtration through an asbestos mat, and the filtrate was evaporated until lead nitrate began to separate. As soon as the solution was cold the mother liquor was poured off and the crystals were centrifugally drained and washed several times with nitric acid. The product was then four times crystallized in quartz, by solution in hot water and precipitation with nitric acid as previously described (see page 1033). Again the crystals were dissolved, and the solution was filtered through a platinum sponge crucible, held in a platinum thistle tube, into a platinum dish, and the salt was three more times crystallized in platinum. Evidence that the material was amply pure before the process was complete was obtained by preparing metallic electrodes from a portion of the five times crystallized material and photographing the spark spectrum. No lines could be seen which were not produced also by the pure specimens of lead prepared previously.¹

A well crystallized specimen of galena from Joplin, Missouri, U. S. A., served as the source of Sample G. A few adherent crystals of zinc blende were mechanically dislodged and the galena was crushed in a large iron mortar. The powder was then digested hot with an excess of 5 *N* nitric acid, and the residue of sulfur, lead sulfate and undecomposed galena was removed by filtration. Since the supply of material was ample the residue was rejected. The filtrate was evaporated until lead nitrate began to separate, and was allowed to cool. After centrifugal separation and rinsing, the crystals were dissolved in water and the solution was filtered

¹ Although Richards and Lambert found the spectrum of radioactive lead to be indistinguishable from that of common lead, there is no reason to expect that ordinary impurities could not be detected in this way.

through an asbestos mat to remove traces of lead sulfate. Four crystallizations in quartz and two in platinum, with intermediate filtration through platinum sponge, followed. The spectrum of metal prepared from the four times crystallized salt was found to show no sign of foreign metals.

A second specimen of cerussite from Wallace, Idaho, U. S. A., was purified exactly as Sample E, except that the nitrate was crystallized four times in platinum vessels, instead of seven times. At this point a spectrographic examination failed to bring to light any metallic impurity. This was designated Sample H.

The three foregoing minerals were all obtained from the Harvard Mineralogical Museum.

Through Dr. F. Krantz of Bonn, Germany, a third specimen of cerussite and one of galena, of guaranteed German origin, were secured. The cerussite was obtained from Commern in the Eifel Mountains, Rhenish Prussia. It was purified exactly as Sample H and the final product was tested for impurities spectrographically with negative results. This specimen is designated Sample I.

Argentiferous galena from Grube Holzappel, Nassau, was converted to nitrate by digestion with nitric acid and the nitrate was four times crystallized in platinum. When metal prepared from this purified nitrate was tested spectrographically, the two strong silver lines of wave lengths 3280 and 3383 were visible, although faint, showing that where lead is badly contaminated with silver even more prolonged purification by crystallization of the nitrate is necessary than was here employed. In order to obtain some idea of the proportion of the impurity, about 1 g. of this nitrate was dissolved in water and, after the addition of a small amount of bromide, the solution was examined in a nephelometer. The very slight opalescence was estimated by comparison with a standard to represent about 0.001 mg. of silver, *i. e.*, 0.0002%, an entirely negligible proportion. This nitrate was not further crystallized, but after it had been converted to chloride and the chloride three times crystallized, electrodes prepared from the final material gave not the slightest indication of silver. This was Sample F.

Dr. M. L. Hartmann very kindly furnished material for Sample J. The mineral consisted of yellow wulfenite (PbMoO_4) and red vanadinite ($\text{Pb}_5(\text{VO}_4)_3\text{Cl}$), and had been collected by Dr. Hartmann in the Tucson mountains, Arizona, U. S. A. The crushed mineral was boiled with 6 *N* nitric acid for some hours and a curdy, yellow precipitate together with an insoluble residue was removed by filtration. When the filtrate was evaporated to small volume and allowed to cool, lead nitrate and a curdy precipitate separated. The latter was removed in suspension by washing the lead nitrate with concentrated nitric acid. The nitrate was dissolved, filtered and crystallized twice in Jena glass and, after filtration through

platinum sponge, three times in platinum. No impurities could be detected spectrographically.

Through the kindness of Professor E. P. Kohler a specimen of galena was obtained from Metalline Falls, Washington, U. S. A., where it occurs in glacial boulders. During the treatment of the mineral with nitric acid so much lead sulfate was produced that the latter substance was recovered by boiling with sodium carbonate and solution in nitric acid. The combined material was crystallized once in glass and four times in platinum. In the spectrum of this material the silver lines were very faintly visible, although when tested with bromide in a nephelometer, no opalescence could be detected. Judging from our experience with Sample F, the proportion of silver could not have been as much as 0.0001%, a proportion which surely must have been eliminated during the three crystallizations as chloride. This specimen is Sample K.

The Radioactivity of the Minerals.

All seven minerals were carefully tested for radioactivity in a quantitative gold leaf electroscope. The natural leak of this electroscope was increased forty times by the black oxide of uranium, while no one of the substances examined increased the leak by an amount that could be detected. Since Richards and Lemberg found the radioactive chloride to be several times as active as uranium oxide where the difference in atomic weight amounted to about half a unit, the sensitiveness of the tests for radioactivity was ample for the purpose.

The Purification of Lead Chloride.

Lead chloride was prepared from the purified lead nitrate by precipitation with hydrochloric acid and crystallization of the product. The latter process served to remove not only traces of nitrate included during the precipitation, but also any metallic impurities which might have escaped elimination in the nitrate crystallization. The difficulties due to isomorphism make it desirable in the preparation of salts of a pure metal to crystallize in at least two different forms. As has already been stated, the traces of silver retained by the nitrate of Samples F and K were effectually eliminated in the chloride crystallization.

About 75 g. of nitrate were dissolved in water and the solution was filtered through platinum sponge into a quartz dish. Constant boiling hydrochloric acid which had been freshly distilled through a quartz condenser was then slowly added, with constant stirring, until an excess was present. Chlorine was never freed in the mother liquor. After the precipitate had settled, it was thoroughly washed by decantation with chilled water and was drained in a platinum centrifugal apparatus. The last wash waters, when tested with diphenylamine, were found to be essentially free from nitrate. The salt was next recrystallized either from water or,

because salt crystallized from water was subsequently found to be basic, from very dilute (0.006 *N*) hydrochloric acid, in platinum vessels. The salt was heated to boiling with the solvent in a large platinum still, and, when the solution was nearly saturated, it was poured into a large platinum dish and was cooled with ice. The mother liquor was used to dissolve fresh portions of the salt until all had been recrystallized. Every sample was three times recrystallized except Samples D₂ and E₂, which were twice recrystallized.

The Drying of Lead Chloride.

After preliminary drying in a vacuum desiccator over fused potassium hydroxide the salt was finally fused in a current of dry hydrochloric acid gas. Experiments described later showed that in the desiccator the moisture content was reduced to a few hundredths of a per cent.

The apparatus for fusing the salt has been used for some years for a similar purpose. Hydrochloric acid gas was generated by dropping concentrated sulfuric acid into fuming hydrochloric acid solution, and was scrubbed and dried by passing through five towers containing beads moistened with concentrated sulfuric acid. All the sulfuric acid previous to use was heated to fuming. Nitrogen was prepared by the Wanklyn process as previously described in this paper, except that the small amount of hydrogen resulting from the catalytic decomposition of the ammonia was not removed. Air also was purified and dried as previously described.

The fusion of the salt was conducted in a platinum or quartz boat in a quartz tube which formed part of a bottling apparatus. After the salt had been gradually heated in a current of hydrochloric acid gas up to the melting point, the acid gas was then displaced by nitrogen and this finally by air. Then the boat and contents were transferred to the weighing bottle in which the boat had been initially weighed, and the system was reweighed.

The Neutrality of Fused Lead Chloride.

In the earlier investigations by Baxter and Wilson, since the lead chloride which had been fused in hydrochloric acid was found to give a clear solution, the assumption was made that the fused salt was neutral. In preliminary experiments in this research, however, upon attempting to dissolve the fused salt in hot water a considerable quantity of white insoluble material separated as soon as the concentration of the solution became high. Similar insoluble material was eventually found to be soluble in acid and to contain chlorine and therefore to be basic chloride. A marked difference between the two cases exists, however. In Baxter and Wilson's experiments the total concentration of salt was never more than half as great as in these preliminary experiments. So far as analysis

of the salt was concerned no difficulty was introduced, for if the water in which the salt is dissolved is acidified slightly at the outset, no insoluble material separates. In these respects lead chloride resembles the bromide very closely. The question is so important, however, that much time was spent in proving that the fused salt really is neutral, and that the basic salt is formed by hydrolysis during solution.

In the first place we established the fact that unfused lead chloride which has been crystallized from dilute hydrochloric acid solution, and which therefore must have been either neutral or possibly slightly acid, when dissolved in water to yield a nearly saturated solution at room temperature, is slightly hydrolyzed to give a precipitate of basic salt. Lead chloride, which has been crystallized from water solution, behaves in the same way, but this is due in part to the fact that such material is already basic at the outset, as will presently be shown. Thus it was proved that the basic salt resulting from solution of fused lead chloride in water was at least in part due to hydrolysis during solution.

The second question as to whether a *portion* of the insoluble material was originally contained in the fused salt was more difficult to settle. The problem was finally solved by the method already employed by Richards¹ to determine the neutrality of fused barium chloride. The procedure was as follows: Two portions of lead chloride which had been crystallized from very dilute hydrochloric acid and dried for some time in a vacuum desiccator, were weighed out simultaneously. These crystals had been ground in an agate mortar during the drying in order to break open inclusions of mother liquor. One portion was dissolved in water with the addition of a trace of nitric acid and was analyzed by comparison with silver in the usual fashion, the details of which will be given shortly. The second portion was carefully fused in hydrochloric acid gas, bottled and weighed. A small quantity of material which sublimed from the boat into the tube was dissolved in water and, after evaporation of the solution in a weighed platinum crucible, the weight of residue was determined. This sublimate was kept as small as possible by taking care to heat the salt barely to the fusion point in a slow current of gas. From the loss in weight during fusion, corrected for the weight of the sublimate, the percentage of moisture in the original material could be ascertained. The fused specimen also was dissolved and compared with silver. Obviously, if no hydrolysis occurs during fusion of the chloride, the ratio of the fused chloride to silver should be the same as the ratio of the unfused, after correction for moisture content.

The data for two parallel pairs of experiments are given below. The analyses of the fused salt appear also in the final tables.

¹ *Proc. Amer. Acad.*, 29, 55 (1893).

| | I. Fused salt. | II. Fused salt. |
|-------------------------------------|-------------------|--------------------|
| Wt. unfused PbCl_2 | 5.26117 g. | 4.17817 g. |
| Wt. fused PbCl_2 | 5.25898 | 4.17472 |
| Loss on fusion..... | 0.00219 | 0.00345 |
| Wt. sublimate..... | 0.00111 | 0.00180 |
| Wt. water..... | 0.00108 | 0.00165 |
| Percentage of water..... | 0.0206 | 0.0396 |
| Wt. black residue..... | 0.00016 g. | 0.00027 g. |
| Corrected wt. PbCl_2 | 5.25882 | 4.17445 |
| Wt. Ag..... | 4.07933 | 3.23862 |
| $\text{PbCl}_2 : 2\text{Ag}$ | 1.28914 | 1.28896 |

Mean, 1.28905.¹

| | Unfused salt. | Unfused salt. |
|---|---------------|---------------|
| Wt. unfused PbCl_2 | 5.82713 g. | 5.65341 g. |
| Wt. moisture (calculated)..... | 0.00120 | 0.00224 |
| Corrected wt. unfused PbCl_2 | 5.82593 | 5.65117 |
| Wt. Ag..... | 4.51915 | 4.38382 |
| $\text{PbCl}_2 : 2\text{Ag}$ | 1.28917 | 1.28910 |

Mean, 1.28914.

The difference between the mean ratio of fused and unfused salt to silver corresponds to an excess of chlorine of 0.0001 g. in the fused salt or an equal deficiency in the unfused material. Because of some uncertainty in the correction for residual moisture in the unfused salt, closer concordance could hardly be expected. The results prove, as far as the method allows, that lead chloride which has been carefully fused in a current of dry hydrochloric acid gas contains no appreciable amount of basic salt.

In connection with the foregoing experiments similar ones were carried out with lead chloride which had been crystallized from water solution. Since these experiments showed first that the salt thus prepared contains basic material, and second that this basic chloride is converted to the neutral salt by fusion in hydrochloric acid gas, the experiments are discussed below in detail. The method of procedure was exactly similar to that described above.

A complication in computing the percentage of water in the unfused salt from the change in weight during fusion is introduced by the fact that when the basic salt contained in the unfused material is fused in hydrochloric acid, hydroxyl (or possibly oxygen) is replaced by chlorine. Thus the water content of the salt is equal to the loss in weight during fusion plus the gain in weight due to replacement of hydroxyl by chlorine. A first approximation to the latter increase in weight was calculated from the apparent deficiency of chlorine found in the comparison of the unfused chloride with silver. Then a more nearly correct value for the water

¹ This happens also to be the mean of 17 experiments, including these two, subsequently recorded.

content was calculated. The whole process of approximation was eventually repeated three times in order to find the water content of the unfused basic chloride to 0.01 mg.

| | I. Fused salt. | II. Fused salt. |
|--|----------------------|----------------------|
| Wt. unfused PbCl_2 | 6.26260 g. | 3.80729 g. |
| Wt. fused PbCl_2 | 6.25929 | 3.80525 |
| Loss on fusion..... | 0.00333 | 0.00204 |
| Wt. sublimate..... | 0.00108 | 0.00106 |
| Gain from replacement of OH by Cl..... | 0.00050 | 0.00056 |
| Water content..... | 0.00273 | 0.00154 |
| Percentage of water..... | 0.0437 | 0.0405 |
| Wt. black residue..... | 0.00045 g. | |
| Corrected wt. PbCl_2 | 6.25884 | |
| Wt. Ag..... | 4.85584 | |
| $\text{PbCl}_2 : 2\text{Ag}$ | 1.28893 ¹ | 1.28908 ² |

Mean of four analyses, 1.28904.

| | Unfused salt. | Unfused salt. |
|---|---------------|---------------|
| Wt. unfused PbCl_2 | 6.14944 g. | 6.34462 g. |
| Wt. water (calculated)..... | 0.00268 | 0.00257. |
| Corrected wt. unfused PbCl_2 | 6.14676 | 6.34205 |
| Wt. Ag..... | 4.76557 | 4.91435 |
| $\text{PbCl}_2 : 2\text{Ag}$ | 1.28983 | 1.29052 |

Mean, 1.29017.

In the four analyses in which the original salt had been crystallized from water previous to fusion, (Analyses 32, 33, 34 and 35) the average ratio of fused salt to silver is 1.28904, a value essentially in agreement with the average of experiments where the salt was crystallized from dilute hydrochloric acid, 1.28905.

These results indicate: first, that owing to hydrolysis lead chloride which has been crystallized from water contains roughly 0.1% less chlorine than the neutral salt and, second, that during fusion in hydrochloric acid gas, material originally basic becomes neutral, a result which cannot be attained with many chlorides such as those of zinc and magnesium.

The Analysis of Lead Chloride.

After the lead chloride had been fused and weighed, the boat and contents were placed in a two liter Erlenmeyer flask, the neck of which was provided with a column of bulbs to catch spray and to serve as a condenser, and was covered with about a liter of distilled water to which 0.1 cc. concentrated nitric acid had been added to prevent the precipitation of the basic salt. The flask and contents were then heated upon an electric stove until the salt was dissolved.

By actually distilling a lead chloride solution of concentration similar

¹ Analysis 35, page 1057.

² The salt which was used in the water determination was lost. This value is the average from three other specimens of similar material (Analyses 32, 33 and 34).

to the analyses (5 g. per liter) with different amounts of nitric acid, it was found that even 4 cc. of nitric acid did not cause an appreciable loss of chlorine.

A slight black insoluble residue of carbon and silica was left floating upon the surface of the solution, as in the case of the bromide. This was collected upon a platinum sponge crucible and determined as described on p. 1041. The average proportion of insoluble residue in twenty-one analyses was 0.004%. The weight of the residue was subtracted from the weight of salt.

The comparison of the lead chloride solutions with silver was effected almost exactly as in the analysis of the bromide (see p. 1041). The concentration of the chloride solution at the time of precipitation was nearly 0.03 *N*, that of the silver solution 0.05 *N*. In Analyses 34 and 36 the chloride solution was poured into the silver solution; in all the others the reverse method of precipitation was employed. No attempt was made to collect the silver chloride in the experiments for comparing the lead chloride with silver.

In the first eight analyses, after the solutions had stood in contact with the precipitated silver chloride for nearly a week with occasional shaking, they were cooled to 0° previous to testing in a nephelometer for excess of chloride or silver, and maintained at that temperature until equivalence of chloride and silver had been reached. Richards and Willard¹ found that the diminution in the solubility of silver chloride thus produced is an assistance in the determination of the end point. In the subsequent analyses this cooling was omitted, since we found that the accuracy of our experiments was not perceptibly increased by the process, which is somewhat troublesome. Needless to say, in the comparison of tubes in the nephelometer, readings were taken until they became constant, and each analysis was tested several times on successive days after the end point had been reached. In the last six analyses two pairs of tubes were always prepared and examined at the same time. Even at the large volume of the analyses the effect of the addition of 0.1 mg. of silver could be detected without cooling to 0°.

During the first two weeks very slight variations in the end point sometimes took place, probably owing to the extraction of occluded chloride or silver. At the end of three weeks no perceptible change was occurring and Analyses 32 and 48 were allowed to stand six weeks without the production of any alteration in the end point from the one found at the end of the third week.

In four separate experiments the silver chloride precipitated by adding an excess of silver nitrate to the solution of the salt was collected and weighed. The lead chloride solution was prepared as previously described

¹ *Pub. Car. Inst.*, 125, 15 (1910); *THIS JOURNAL*, 32, 16 (1910).

and was precipitated by adding a solution of a weighed, very nearly equivalent amount, of very pure silver nitrate containing several cubic centimeters of nitric acid. In Analyses 49 and 52 the silver nitrate solution was added to the chloride solution; in Analyses 50 and 51 the reverse method of precipitation was followed. The precipitate was left in contact with the mother liquor for two weeks, with occasional shaking, in order to allow occluded material to be extracted. Then an excess of 0.05 g. silver nitrate for each liter of mother liquor was added, and after a day's standing the precipitate was washed and collected upon a large weighed platinum-sponge crucible. The precipitate was washed twelve times with silver nitrate solution containing 0.05 g. per liter and once with chilled water before transference to the crucible with ice cold water.

The crucible and contents were dried at 235° for sixteen hours in an electrically heated porcelain air bath before they were weighed. In order to determine how much moisture was retained by the dried chloride, it was transferred to a small porcelain crucible and weighed, then heated to fusion inside a larger crucible and again weighed. The loss in weight, which represents the moisture expelled, was never more than 0.002% of the weight of the salt. Although the dried, unfused salt was superficially very slightly discolored, the fused material was colorless.

A correction of 0.05 mg. per liter was applied for silver chloride dissolved in the mother liquor and silver nitrate wash waters. This correction is calculated from the solubility product of silver chloride at 20° as determined by Kohlrausch,¹ 1.0×10^{-10} . The silver chloride dissolved in the aqueous washings together with that dissolved from the precipitation flask by rinsing with ammonia was estimated by nephelometric comparison in each experiment. This never amounted to more than 0.75 mg. per liter.

Vacuum corrections for lead chloride and silver chloride were applied by adding 0.000060² and 0.000071 g., respectively, for each apparent gram of substance.

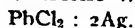
Results and Discussion.

It is obvious that there is no evidence of dissimilarity in the various samples of chloride. The extreme difference in Series III, 0.04 unit, corresponds to less than 0.0006 g. of silver or 0.0007 g. of lead chloride, with a 5 g. portion of chloride. In Series IV, with larger quantities of lead chloride the extreme difference is half as large, corresponding to 0.0005 g. of silver chloride and to the same amount of lead chloride. The agreement of the averages with different specimens of lead chloride is even better.

¹ *Z. physik. Chem.*, 64, 147 (1908).

² Computed from the density 5.89, recently found in this laboratory at 25° by Mr. C. F. Hawkins.

SERIES III.—THE ATOMIC WEIGHT OF LEAD.



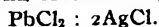
Ag = 107.880.

Cl = 35.457.

| Number of analysis. | Sample of PbCl_2 . | Wt. of PbCl_2 in vacuum. Grams. | Wt. of residue. Milligram. | Corr. wt. of PbCl_2 in vacuum. Grams. | Wt. of Ag in vacuum. Grams. | Wt. of Ag added. Milligram. | Corr. wt. of Ag in vacuum. Grams. | Ratio $\text{PbCl}_2 : 2\text{Ag}.$ | At. wt. of Pb. |
|---------------------|-----------------------------|--|----------------------------|--|-----------------------------|-----------------------------|-----------------------------------|-------------------------------------|----------------|
| 32 | D ₂ | 5.63594 | 0.27 | 5.63567 | 4.37235 | —0.35 | 4.37200 | 1.28904 | 207.21 |
| 33 | D | 5.58758 | 0.28 | 5.58730 | 4.33467 | —0.40 | 4.33427 | 1.28910 | 207.22 |
| 34 | D | 6.86348 | 0.29 | 6.86319 | 5.32382 | +0.20 | 5.32402 | 1.28910 | 207.22 |
| | | | | | | | Average, | 1.28908 | 207.22 |
| 35 | E ₂ | 6.25929 | 0.45 | 6.25884 | 4.85564 | +0.20 | 4.85584 | 1.28893 | 207.19 |
| 36 | E | 5.25898 | 0.16 | 5.25882 | 4.07968 | —0.35 | 4.07933 | 1.28914 | 207.23 |
| | | | | | | | Average, | 1.28904 | 207.21 |
| 37 | F | 5.73451 | 0.17 | 5.73434 | 4.44877 | —0.20 | 4.44857 | 1.28903 | 207.21 |
| 38 | F | 4.17472 | 0.27 | 4.17445 | 3.23837 | +0.25 | 3.23862 | 1.28896 | 207.19 |
| | | | | | | | Average, | 1.28900 | 207.20 |
| 39 | G | 4.70784 | 0.14 | 4.70770 | 3.65198 | +0.25 | 3.65223 | 1.28899 | 207.20 |
| 40 | G | 4.20234 | 0.12 | 4.20222 | 3.25965 | +0.03 | 3.25968 | 1.28915 | 207.23 |
| | | | | | | | Average, | 1.28907 | 207.22 |
| 41 | H | 7.04713 | 0.25 | 7.04688 | 5.46697 | —0.06 | 5.46691 | 1.28901 | 207.20 |
| 42 | H | 5.88935 | | 5.88935 ¹ | 4.56888 | —0.20 | 4.56868 | 1.28907 | 207.22 |
| | | | | | | | Average, | 1.28904 | 207.21 |
| 43 | I | 6.57246 | 0.30 | 6.57216 | 5.09849 | 0.00 | 5.09849 | 1.28904 | 207.21 |
| 44 | I | 5.66347 | 0.17 | 5.66330 | 4.39340 | 0.00 | 4.39340 | 1.28905 | 207.21 |
| | | | | | | | Average, | 1.28905 | 207.21 |
| 45 | J | 4.90098 | 0.15 | 4.90083 | 3.80188 | —0.17 | 3.80171 | 1.28911 | 207.22 |
| 46 | J | 5.79313 | 0.13 | 5.79300 | 4.49404 | 0.00 | 4.49404 | 1.28904 | 207.21 |
| | | | | | | | Average, | 1.28908 | 207.22 |
| 47 | K | 5.43992 | 0.27 | 5.43965 | 4.21992 | 0.00 | 4.21992 | 1.28904 | 207.21 |
| 48 | K | 5.74557 | 0.53 | 5.74504 | 4.45584 | +0.90 | 4.45674 | 1.28907 | 207.22 |
| | | | | | | | Average, | 1.28906 | 207.21 |
| | | | | | | | Average of individual analyses, | 1.28905 | 207.21 |

¹ Undetermined, but wholly negligible.

SERIES IV.—THE ATOMIC WEIGHT OF LEAD.



Ag = 107.880.

Cl = 35.457.

| Number of analysis. | Sample of PbCl_2 . | Wt. of PbCl_2 in vacuum. Grams. | Wt. of residue. Milligram. | Corr. wt. of PbCl_2 in vacuum. Grams. | Wt. of AgCl in vacuum. Grams. | Loss on fusion. Milligram. | Dissolved AgCl . Milligram. | Corr. wt. of AgCl in vacuum. Grams. | Ratio $\text{PbCl}_2 : 2\text{AgCl}.$ | At. wt. of Pb. |
|---------------------|-----------------------------|--|----------------------------|--|--|----------------------------|--------------------------------------|--|---------------------------------------|----------------|
| 49 | H | 6.96405 | 0.35 | 6.96370 | 7.17708 | 0.14 | 0.60 | 7.17754 | 0.97021 | 207.22 |
| 50 | H | 6.89063 | 0.17 | 6.89046 | 7.10147 | 0.08 | 0.92 | 7.10231 | 0.97017 | 207.21 |
| | | | | | | | | Average, | 0.97019 | 207.21 |
| 51 | E | 7.33259 | 0.32 | 7.33227 | 7.55609 | 0.10 | 1.33 | 7.55732 | 0.97022 | 207.22 |
| 52 | E | 6.51730 | 0.31 | 6.51699 | 6.71604 | 0.14 | 1.00 | 6.71690 | 0.97024 | 207.23 |
| | | | | | | | | Average, | 0.97023 | 207.23 |
| | | | | | | | | Average of individual analyses, | 0.97021 | 207.22 |
| | | | | | | | | Average of Series III and IV, | | 207.21 |

¹ In this experiment the residue was so small that it was not determined.

The average of Series III is very slightly lower than that of Series IV. The difference, 0.01 unit, indicates a slight deficiency in the weight of silver chloride or a slight excess in the weight of silver or both. However, at the most the discrepancy corresponds to less than 0.0003 mg. of substance.

In the following table a more complete comparison of the different specimens of material is made:

| Sample of PbCl ₂ | Mineral. | Source. | Series III. PbCl ₂ :2Ag. | Series IV. PbCl ₂ :2AgCl. | Average. |
|--------------------------------|---------------------------|----------------------------------|--|---|----------|
| D | | Commercial nitrate | 207.22 | | 207.22 |
| E | Cerussite | New South Wales, Australia | 207.21 | 207.23 | 207.22 |
| F | Cerussite | Eifel Mts., Germany | 207.20 | | 207.20 |
| G | Galena | Joplin, Mo., U. S. A. | 207.22 | | 207.22 |
| H | Cerussite | Wallace, Id., U. S. A. | 207.21 | 207.21 | 207.21 |
| I | Galena | Nassau, Germany | 207.21 | | 207.21 |
| J | { Vanadinite Wulfenite | Tucson, Ariz., U. S. A. | 207.22 | | 207.21 |
| K | Galena | Metalline Falls, Wash., U. S. A. | 207.21 | | 207.21 |
| Average, 207.21 | | | 207.22 | 207.21 | 207.21 |

In comparing the analyses of the bromide and chloride, variations are found of the same order of magnitude as in the separate series.

| | | Ratio. | Number of analysis. | At. wt. |
|--|--------------------------------|---------|------------------------|---------|
| Series I | PbBr ₂ : 2Ag..... | 1.70111 | 19 | 207.20 |
| Series II | PbBr ₂ : 2AgBr..... | 0.97715 | 11 | 207.18 |
| Series III | PbCl ₂ : 2Ag..... | 1.28905 | 17 | 207.21 |
| Series IV | PbCl ₂ : 2AgCl..... | 0.97021 | 4 | 207.22 |
| Average..... | | | | 207.20 |
| Average, weighted according to number of analyses. | | | | 207.20 |

In all four series the results vary between essentially the same limits, so that the safest method of combining the four series is to compute the arithmetical mean. Weighting the average of each series according to the number of analyses does not alter the value of the mean. Of the four series, those in which the lead halides are compared with silver, Series I and III, are probably, on the whole, less subject to error. These two series agree almost exactly, both with each other and with the average of all four series. This final average, therefore, 207.20, seems to us to represent fairly the result of our work.

One more comparison may very well be made at this point, between the different silver samples. Since it is uncertain whether in the first five analyses Sample I or II of silver was used, these experiments are not included in the table.

| Sample of Ag. | PbBr ₂ : 2Ag. | PbCl ₂ : 2Ag. | Average of individual experiments. |
|---------------|--------------------------|--------------------------|------------------------------------|
| I..... | 207.20 | 207.21 | 207.20 |
| II..... | 207.21 | 207.22 ¹ | 207.21 |
| III..... | 207.18 ¹ | 207.21 | 207.20 |
| IV..... | 207.18 ¹ | 207.21 ¹ | 207.20 |
| | Average, 207.19 | 207.21 | 207.20 |

Here again evidence of dissimilarity in material is lacking.

In comparing the present work with the earlier work of Baxter and Wilson, it is obvious that the discrepancy, 0.1 unit, is larger than the experimental error in either research. We are unable to offer any certain explanation of this difference. It is improbable that in the earlier work the silver chloride was contaminated with occluded material, for the precipitate was carefully examined for lead salts with negative results.² Furthermore, if lead chloride were occluded by the silver chloride, it would have raised the apparent atomic weight of lead, whereas the difference is in the opposite direction. On the whole, less difficulty was experienced in the earlier work than in the later from insoluble residue in the fused salt, for the final material left no visible residue upon solution. It might be suggested that the lead material used in the earlier work actually possessed an atomic weight different from that of any used in the present investigation. This seems unlikely, since no difference could be detected between any of the varied materials examined later. Unfortunately none of the material remained from the first investigation, so that comparison was impossible. Another possibility is that in Baxter and Wilson's experiments, during the fusion of the lead chloride in a current of hydrochloric acid in a glass tube, sufficient alkali chloride sublimed from the glass into the lead salt, or on the boat, to produce the difference. Only 0.025% of sodium chloride or 0.035% of potassium chloride would have been necessary, which represent about a milligram of impurity with a 4-5 gram portion. This seems on the whole the most probable explanation. It must be remembered, however, that because of the high atomic weight of lead, it is far more sensitive to experimental error than is an atomic weight of lesser magnitude. Because of the far larger number of experiments, and the more complete treatment, we feel that the present work should supersede the earlier research, even though the cause of the difference is not wholly certain.

With regard to the bearing of our work upon the theories of atomic disintegration, it is evident that no far-reaching conclusion may be drawn. If lead is a product of radioactive change, it might reasonably be expected to vary in atomic weight according as it originates in uranium or thorium, or both. This seems to be the case only with material extracted from

¹ This is the result of one analysis only.

² *Loc. cit.*, p. 367.

uranium and thorium ores. But this material differs from common lead in still possessing radioactivity, even though spectroscopically the radioactive and common material seem to be identical.¹ It still remains to be finally determined whether it is possible to separate radioactive lead into constituent parts, one of which may be ordinary lead.² It certainly is remarkable, however, if common lead is composed wholly or in part of isotopes of different atomic weights, that the proportions should be as constant in geographically and mineralogically different specimens of material as the constancy in the atomic weight indicates.

It is not at all certain, however, that during the expulsion of the α -particle the weight of the atom undergoes no other change, for as Hönigschmid³ has pointed out, the difference between his own recent determinations of the atomic weights of uranium and radium is not an even multiple of the atomic weight of helium. Possibly, after all, ordinary lead is the end product of the disintegration of uranium or thorium, or both.

At present we are engaged in an attempt to discover a comparative method for the determination of the atomic weight of lead as different as possible from the one employed here.

Summary.

1. Eleven specimens of lead salts from many different geographical and mineralogical sources were purified by various methods, and were found to be identical so far as could be determined by spectroscopic examination and by analysis of the chloride and bromide. None of these specimens were found to be radioactive to an appreciable extent.

2. Electrolytic deposition with a dissolving anode through nitrate or chloride electrolyte was found to be an unsatisfactory method of purifying lead from small amounts of silver and copper. Crystallization of the nitrate proved to be an efficient method.

3. Neutral lead bromide and chloride were found to hydrolyze upon solution in water, with precipitation of basic salts. Lead chloride which had been crystallized from water was found to be basic, although when crystallized from very dilute hydrochloric acid it is neutral.

4. Lead bromide and chloride which had been fused in an atmosphere of dry hydrobromic and hydrochloric acid gases, respectively, were found to be neutral.

5. By the analysis of both lead bromide and lead chloride the atomic weight of common lead was found to be 207.20, if $A_g = 107.880$, or 207.18, if $A_g = 107.870$.

¹ Richards and Lambert, *Loc. cit.*, p. 1341.

² *Ibid.*, p. 1343.

³ *Z. Electrochem.*, 20, 457 (1914). See also Whytlaw-Gray and Ramsay, *Z. physik. Chem.*, 80, 275 (1912).

6. No evidence was found that common lead is composed either wholly or in part of isotopes of different atomic weight.

We are very greatly indebted to the Carnegie Institution of Washington for generous assistance in the pursuit of this investigation.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE VAPOR PRESSURE OF IODINE BETWEEN 50° AND 95°.

BY GREGORY PAUL BAXTER AND MERRITT ROY GROSE.

Received March 1, 1915.

Some years ago the vapor pressure of iodine was determined in the Harvard Laboratory¹ by the "air current" method throughout the temperature range 0° to 55°. This earlier research was interrupted by the end of the college year during attempts to continue the work at still higher temperatures. In the present investigation the difficulties met at the close of the earlier work were overcome and the method has been extended to cover the temperatures up to 95°.

The procedure in general was to pass a measured volume of pure, dry air, first over the pure iodine, and then into a solution of sodium carbonate to absorb the volatilized iodine. From the carbonate solution, after acidification and reduction of the liberated iodine by means of hydrazine, the iodine was precipitated as silver iodide, which was collected and weighed. In the experiments below 55°, sodium sulfite was used to absorb the iodine, but at higher temperatures this proved too easily oxidized by the oxygen of the air current. An aqueous solution of hydrazine did not reduce the iodine rapidly enough, while sodium hydroxide, attacked the glass apparatus very rapidly.

The purification of the iodine was carried out by methods which have been found effective in earlier researches.² Commercial iodine was dissolved in aqueous potassium iodide and distilled from a retort into a Jena flask cooled with running water. The product was several times rinsed with water, and was then suspended in water and reduced to hydriodic acid by means of well scrubbed hydrogen sulfide gas. After being boiled for some time to remove hydrocyanic acid which might have had its source in cyanogen impurity in the iodine, the solution was filtered to remove coagulated sulfur, and was then oxidized in a retort with a slight excess of potassium permanganate. In the latter process there is set free only five-eighths of the iodine, which was then distilled from the solution of potassium and manganous iodides as before. Although this second distillation from an aqueous iodide must have eliminated every trace of

¹ Baxter, Hickey and Holmes, *THIS JOURNAL*, 29, 127 (1907).

² *THIS JOURNAL*, 26, 1577 (1904); 27, 876 (1905).

chlorine and bromine, the product was again reduced with hydrogen sulfide and the hydriodic acid solution was oxidized with recrystallized permanganate. The final product was thoroughly rinsed with water, drained on a perforated porcelain funnel and superficially dried over sulfuric acid for some time.

During the course of the work the tube containing the iodine was several times broken so that the contents were wet with the thermostat water. After such an accident the iodine was redistilled from the final solution of potassium and manganous iodides obtained in the purification of the iodine, which was carefully saved for the purpose. Naturally, rinsing and drying of the iodine followed in each case.

Since iodine which has been dried over sulfuric acid still retains water, the partially dried material was finally distilled in a current of dry air in a hard glass tube. The tube was constricted at three points and the iodine was distilled from porcelain boats into the first section, then into the second and third and finally from the tube into a Jena glass retort. The iodine was gently scraped from the walls of the retort.

Sodium carbonate and silver nitrate were both twice crystallized, the latter from nitric acid solution, in order to remove chlorides.

In order to prepare hydrazine, the sulfate was treated with a solution of a large excess of sodium hydroxide in a platinum retort, and the hydrazine was distilled through a platinum condenser. The product was then redistilled. The approximate concentration of the solution was found by comparison with a standard solution of iodic acid in the presence of sodium acetate.

The air used for the sublimation of the iodine was first passed through a tube filled with hot copper oxide, then through a series of towers, one of which contained beads moistened with a solution of potassium hydroxide containing potassium permanganate; one, silver nitrate solution; and three, concentrated sulfuric acid. The last traces of moisture were removed by resublimed phosphorus pentoxide. The apparatus was constructed wholly of glass. The air used in the vapor pressure experiments was not passed over hot copper oxide, but otherwise was similarly purified.

The apparatus used for saturating the air with iodine and for absorbing the iodine was constructed in very much the same way as that used in the earlier research. A spiral glass tube, of about 1 cm. internal diameter, contained the iodine, which formed a column about 30 cm. long. Air was passed through a ground joint from the purifying train into one end of this tube. The other end of the tube was connected by means of a ground joint with the first absorbing tube containing a concentrated solution of sodium carbonate. A second absorbing spiral containing sodium carbonate solution was fused to the first, and in some experiments a third absorbing tube was attached to the first two by a ground joint.

Since, however, no iodine was ever found in the third absorber, in later experiments it was omitted. During a run, the iodine tube and first absorbing tube, including the connecting joint, were immersed in the water of the thermostat. It was necessary of course that this joint should be both tight and dry. Both results were secured by covering the joint completely with a piece of rubber tube securely wired in place. Since the joint was at the temperature of the thermostat it was to be expected that no iodine would condense between the saturating and first absorbing tube, and this was invariably the case, except in two of the preliminary experiments where a very small amount of solid iodine was found in the joint. The outlet of the iodine tube was constricted to 2 mm. to prevent diffusion into the absorbing bulb.

From the second absorbing tube the air passed into the large aspirator bottle used to produce the air current. This bottle, which had a capacity of more than 8 liters, was provided with a thermometer, an open tube mercury manometer, and an outlet tube through which the water content flowed into a carefully standardized bottle of about 8 liters volume in the experiments at the lower temperatures, of about 5 liters volume in the experiments at the higher temperatures. The rubber stoppers in the upper and lower tubulatures of the aspirator bottle were made tight with grease and in addition were wired in place and covered with shellac. The aspirator bottle was also jacketed with plumbers wool to secure constancy in temperature, and the temperature of the water at the outset was adjusted to that of the room so that no appreciable change in temperature of the water occurred during an experiment. The temperature of the room itself was controlled within a very few degrees by a thermostat.

The thermostat had a capacity of 25 liters, and was jacketed with an inch of plumbers wool. The greater part of the necessary heat was furnished by a burner under the thermostat tank, but the fine adjustment of temperature was secured by an incandescent light bulb controlled by a mercury-toluene regulator in the usual way. A mechanical stirrer proved very efficient in preventing variations in temperature in different parts of the bath. In order to avoid disturbances from evaporation at the surface of the bath, in experiments above 70° the water was covered with a layer of paraffine, which also reduced greatly the heat necessary to operate the bath and prevented unpleasant humidity in the laboratory even at 95°.

The corrections of the thermometers were found to hundredths of a degree by comparison with one standardized by the Physikalisch-Technische Reichsanstalt, due allowance being made for the exposed thread.

The procedure of an experiment was the usual one. After the apparatus had been connected, and the iodine tube with the first absorbing tube containing nearly saturated sodium carbonate solution had been allowed

to come to the temperature of the thermostat, the aspirator was started. No water was collected from the aspirator bottle, however, until air began to bubble through the sodium carbonate solution in the first absorbing bulb. At this point the reading of the manometer in the aspirator bottle was taken and at the end of the experiment the pressure in the aspirator bottle was brought to exactly the same point. The temperature of the water in the aspirator also was noted. When the receiving bottle was full of water, its temperature was taken and if this temperature was different from the initial temperature of the aspirator, a correction was applied to the volume of the water. The difference was never more than 2° . At the end of the experiment the temperature of the air in the aspirator bottle was read and also the barometric pressure upon a Green barometer.

As soon as the absorbing tubes had been disconnected from the iodine tube at the close of an experiment, a small amount of hydrazine was added to the absorbing tube nearest the iodine tube. This served to collect any iodine vapor still unabsorbed and to decolorize the absorbing solution, which in experiments at higher temperatures was usually somewhat brown.

As the temperature rose the amount of carbon dioxide freed by the action of the iodine upon the sodium carbonate became appreciable. Some of this undoubtedly was held by the cold sodium carbonate solution in the second absorbing bulb, and some was dissolved in the water of the aspirator bottle. In order to remove this carbon dioxide a bulb containing a solution of potassium hydroxide was inserted in the aspirating system between the second absorbing bulb and the aspirator bottle in many of the experiments at 80° and above. Even at 85° it was doubtful whether any real benefit was produced by the potassium hydroxide bulb, so that it is certain that its omission at the lower temperatures introduced no error. At 90° the experiments in which the above precaution was taken yielded somewhat higher results, as would be expected.

The carbonate solution from both absorbing bulbs was rinsed into a large glass stoppered Erlenmeyer flask and an excess of hydrazine was added. Dilute nitric acid in slight excess was next slowly introduced through a funnel extending to the bottom of the solution. As soon as the brown color indicating an excess of acid appeared the flask was tightly stoppered and left till colorless. Then more nitric acid was added, and if any further quantity of iodine separated, the flask was again closed and left till colorless. Care was taken to prevent free iodine from reaching the surface of the solution until the flask was stoppered.

A very dilute solution of a slight excess of pure silver nitrate was used to precipitate the iodine. A large excess was avoided because of the danger of the occlusion of the silver nitrate by the iodine.¹ After long standing

¹ K \ddot{o} thner and Aeuer, *Lieb. Ann.*, 337, 123 (1905); Baxter, *THIS JOURNAL*, 27, 880 (1905).

the precipitate was washed with water and collected upon a platinum-sponge Gooch crucible. It was dried at 180° in an electric oven before being weighed.

Calculation of the results was carried out as follows:

From the weight of silver iodide the weight of volatilized iodine was determined. The volume of this iodine as vapor was then calculated upon the assumption that 253.9 g. of iodine at 0° and 760 mm. would occupy 22.40 liters. The volume of air into which this iodine vaporized was reduced to the same conditions by means of the following formula:

$$V = v \frac{(B - h - m)}{760} \frac{273}{t + 273}$$

in which

v = corrected volume of water run out.

B = barometric reading corrected to 0°.

h = vapor pressure of water at the final temperature of the aspirator.

m = diminution in pressure indicated by the manometer.

t = final temperature of the aspirator.

Since the pressure within the iodine tube was that of the room,¹ the vapor pressure of iodine is then equal to

$$\frac{\text{volume of iodine vapor}}{\text{volume of iodine} + \text{volume of air}} \times \text{barometric pressure.}$$

This method of calculation involves the following assumptions:

1. That no solvent effect is exerted by air upon iodine.
2. That one mole of iodine has a volume of 22.40 liters.

It is well known that in the cases of chlorine and bromine at ordinary temperatures and pressures molecular quantities of these elements occupy considerably less than the theoretical volumes. Furthermore V. Meyer² found that at 253° the density of iodine vapor compared with air is 8.86, whence the volume of a mole is 22.2 liters. However, since in our experiments the pressure of the iodine vapor was low even at the higher temperatures, the above assumption seems safe.

Crafts and Meier,³ have found experimentally that iodine vapor is essentially undissociated at the boiling point of sulfur. Hence, it is improbable that, even at the great dilution of the iodine vapor in our experiments, any measurable dissociation could have taken place.

The bottles in which the water was measured were standardized by filling them from a standardized liter flask, after they had been wet with water and allowed to drain. Previous to use they were allowed to drain the same length of time. The cubical coefficient of expansion of glass is

¹ This was shown by a manometer located immediately before the iodine tube.

² *Ber.*, 13, 397 (1880).

³ *Ibid.*, 13, 861 (1880).

so small, 0.0025%, that no correction is necessary for the slight differences between the temperature of standardization and that of experiment.

In order to make sure that complete saturation of the air with iodine was attained, the rate at which the air was passed through the tube was varied in different experiments within wide limits, the time required for a volume of a liter being in some cases as small as one-half hour and sometimes as much as an hour. The velocity of the air current shows no apparent influence.

Weights were standardized to tenths of a milligram, and a vacuum correction of +0.00007 g. was applied to the larger weights of silver iodide.

TABLE I.—THE VAPOR PRESSURE OF IODINE.

| Temperature centigrade. Degrees. | Rate per hour. L. | Volume of air corr. to 0° and 760 mm. Cc. | Barometric pressure corr. to 0°. Mm. | Weight of AgI. G. | Vapor pressure of iodine. Mm. |
|--|-------------------------|--|---|-------------------------|--|
| 50 | 1.6 | 7152 | 765.3 | 0.4222 | 2.149 |
| 50 | 1.6 | 7025 | 753.3 | 0.4218 | 2.151 |
| 50 | 1.6 | 7183 | 763.2 | 0.4279 | 2.163 |
| | | | | Mean, | 2.154 |
| 55 | 2.0 | 6917 | 746.1 | 0.5973 | 3.061 |
| 55 | 1.1 | 7034 | 759.0 | 0.5984 | 3.067 |
| 55 | 1.2 | 7019 | 761.7 | 0.5973 | 3.079 |
| 55 | 1.5 | 7238 | 758.9 | 0.6173 | 3.075 |
| 55 | 1.3 | 7059 | 751.9 | 0.6049 | 3.061 |
| | | | | Mean, | 3.069 |
| 60 | 1.6 | 7123 | 751.3 | 0.8517 | 4.261 |
| 60 | 1.7 | 6635 | 744.0 | 0.8064 | 4.288 |
| 60 | 1.3 | 7175 | 749.7 | 0.8710 | 4.316 |
| 60 | 1.5 | 7124 | 758.8 | 0.8453 | 4.271 |
| 60 | 2.0 | 6161 | 749.2 | 0.7457 | 4.300 |
| 60 | 1.0 | 7116 | 754.6 | 0.8497 | 4.273 |
| 60 | 1.2 | 7057 | 745.6 | 0.8551 | 4.284 |
| | | | | Mean, | 4.285 |
| 65 | 1.5 | 7169 | 762.7 | 1.1819 | 5.951 |
| 65 | 1.8 | 6979 | 751.2 | 1.1660 | 5.939 |
| 65 | 1.3 | 7087 | 767.8 | 1.1655 | 5.976 |
| 65 | 1.0 | 7211 | 762.8 | 1.1919 | 5.967 |
| 65 | 2.0 | 7267 | 770.2 | 1.1916 | 5.977 |
| | | | | Mean, | 5.962 |
| 70 | 1.2 | 7227 | 768.6 | 1.6422 | 8.242 |
| 70 | 1.6 | 7243 | 765.3 | 1.6531 | 8.241 |
| 70 | 1.2 | 7183 | 763.5 | 1.6310 | 8.180 |
| 70 | 1.8 | 7167 | 765.3 | 1.6400 | 8.263 |
| 70 | 1.3 | 7230 | 770.2 | 1.6245 | 8.167 |
| 70 | 1.5 | 7048 | 746.6 | 1.6274 | 8.133 |
| 70 | 1.0 | 6267 | 757.6 | 1.4299 | 8.156 |
| 70 | 1.8 | 7136 | 761.0 | 1.6276 | 8.190 |
| 70 | 1.1 | 7135 | 760.4 | 1.6299 | 8.196 |
| 70 | 1.6 | 7097 | 757.5 | 1.6262 | 8.189 ¹ |
| | | | | Mean, | 8.196 |

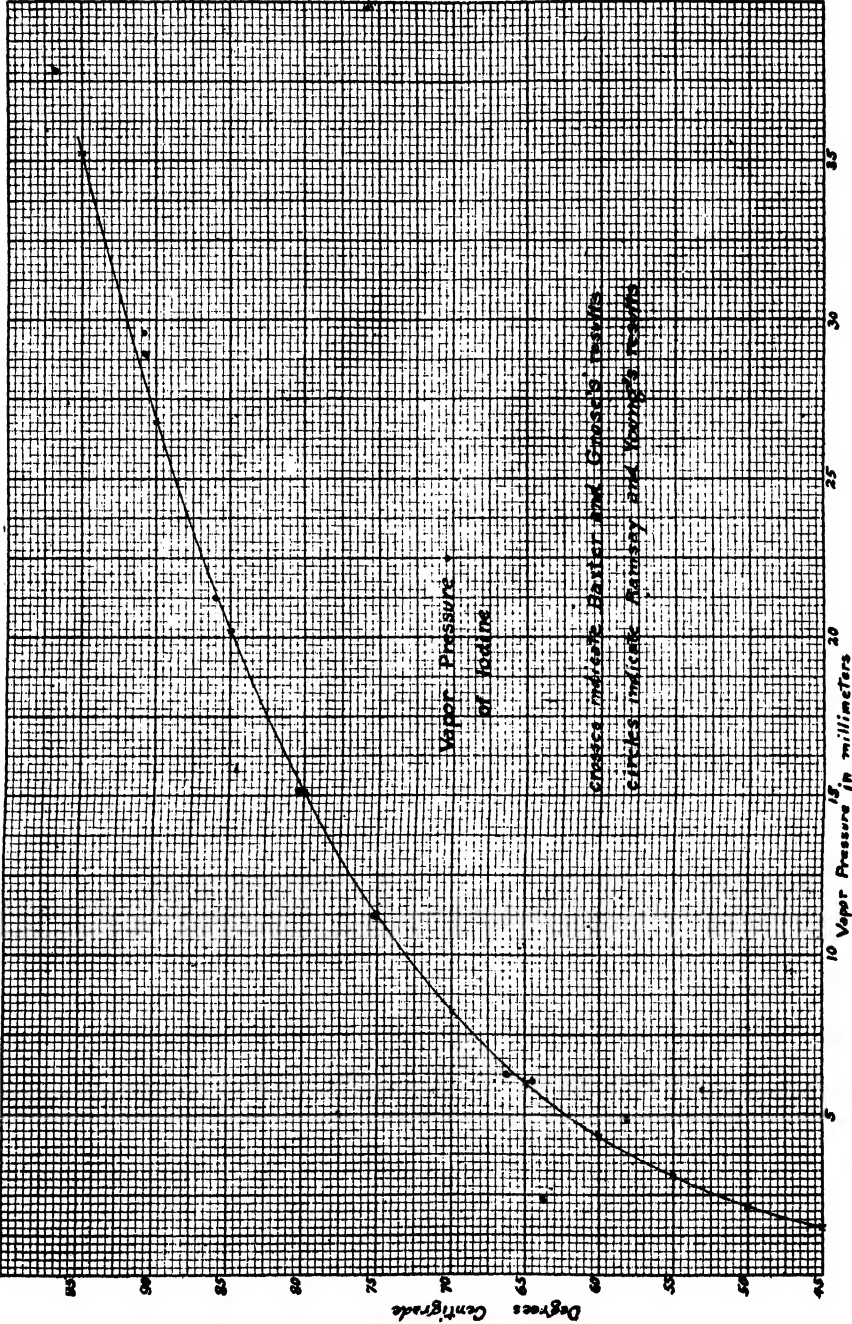
¹ KOH bulb used.

TABLE I.—THE VAPOR PRESSURE OF IODINE (*continued*).

| Temperature centigrade. Degrees. | Rate per hour. L. | Volume of air corr. to 0° and 760 mm. Cc. | Barometric pressure corr. to 0°. Mm. | Weight of AgI. G. | Vapor pressure of iodine. Mm. |
|--|-------------------------|--|---|-------------------------|--|
| 75 | 1.2 | 7064 | 762.2 | 2.2046 | 11.18 |
| 75 | 1.2 | 7151 | 760.0 | 2.2409 | 11.19 |
| 75 | 1.2 | 6885 | 739.2 | 2.2327 | 11.26 |
| 75 | 1.2 | 7082 | 753.5 | 2.2385 | 11.19 |
| 75 | 1.0 | 7154 | 763.7 | 2.2414 | 11.24 |
| Mean, | | | | | 11.21 |
| 80 | 1.4 | 4620 | 761.3 | 1.9568 | 15.08 |
| 80 | 1.3 | 4641 | 769.4 | 1.9438 | 15.07 |
| 80 | 1.1 | 7170 | 759.7 | 3.0461 | 15.09 |
| 80 | 1.4 | 4674 | 774.0 | 1.9473 | 15.08 |
| 80 | 2.0 | 7188 | 760.9 | 3.0486 | 15.09 |
| 80 | 1.4 | 4564 | 755.3 | 1.9559 | 15.13 ¹ |
| 80 | 1.5 | 4582 | 760.5 | 1.9442 | 15.09 ¹ |
| 80 | 1.7 | 4545 | 770.6 | 1.9024 | 15.08 ¹ |
| Mean, | | | | | 15.09 ¹ |
| 85 | 1.0 | 4606 | 762.0 | 2.6079 | 20.04 |
| 85 | 1.9 | 4563 | 757.1 | 2.6205 | 20.19 |
| 85 | 1.9 | 4585 | 764.6 | 2.6057 | 20.18 |
| 85 | 1.7 | 4573 | 755.3 | 2.6421 | 20.26 |
| 85 | 1.9 | 4608 | 761.7 | 2.6390 | 20.25 |
| 85 | 1.3 | 4499 | 755.5 | 2.6066 | 20.32 ¹ |
| 85 | 1.2 | 4595 | 767.2 | 2.6011 | 20.17 ¹ |
| 85 | 1.5 | 4379 | 758.7 | 2.5067 | 20.16 ¹ |
| Mean, rejecting the first, | | | | | 20.21 |
| 90 | 1.3 | 4645 | 765.2 | 3.5377 | 26.82 ¹ |
| 90 | 1.1 | 4614 | 762.1 | 3.5371 | 26.88 ¹ |
| 90 | 1.3 | 4542 | 762.3 | 3.4489 | 26.65 ¹ |
| Mean, | | | | | 26.78 |
| 95 | 1.4 | 4583 | 764.7 | 4.6367 | 35.20 ¹ |
| 95 | 1.5 | 4605 | 771.3 | 4.6310 | 35.31 ¹ |
| 95 | 1.5 | 4551 | 762.0 | 4.6215 | 35.21 ¹ |
| Mean, | | | | | 35.24 |

At 50° the vapor pressure of iodine, 2.154 mm., agrees exactly with that previously found by Baxter, Hickey and Holmes. At 55° the value found here is slightly lower, but that is not surprising, because in the earlier work difficulty was experienced above 50° from separation of iodine at the ground joint between the iodine tube and the first absorbing tube. Our results are uniformly lower than those of Wiedermann, Stelzner and Niedershulte.² The curve plotted with our values against the temperature (Curve 1) makes a very satisfactory extension of the one obtained by Baxter, Hickey and Holmes, and is not very different from that plotted

¹ KOH bulb used.² *Verh. phys. Ges.*, 3, 159 (1905).



Curve 1.

with Ramsay and Young's¹ results over the same temperature range, thus giving a very satisfactory comparison of a static and a dynamic method.

Many attempts were made to find a mathematical relationship between vapor pressure and temperature, and two of these were successful enough to warrant drawing attention to them. If the logarithm of the vapor pressure is plotted against the logarithm of the absolute temperature, the result is not far from a straight line. This curve can be represented very closely by the equation

$$\log p = -106.3930 + 46.611 \log T - 0.031677 T$$

which differs from the thermodynamic equation developed by Clausius only in that the absolute temperature appears in the numerator instead of the denominator of the last term. The results obtained with this equation over the range 0-95° are given in Table II.

TABLE II.

| Temperature centigrade. Degrees. | Vapor pressure calculated. Mm. | Vapor pressure observed. Mm. | Difference. Mm. | Temperature centigrade. Degrees. | Vapor pressure calculated. Mm. | Vapor pressure observed. Mm. | Difference. Mm. |
|--|---|---------------------------------------|--------------------|--|---|---------------------------------------|--------------------|
| 0 | 0.032 | 0.030 | +0.002 | 60 | 4.285 | 4.285 | 0.000 |
| 15 | 0.131 | 0.131 | 0.000 | 65 | 5.962 | 5.962 | 0.000 |
| 25 | 0.311 | 0.305 | +0.006 | 70 | 8.210 | 8.196 | +0.014 |
| 30 | 0.469 | 0.469 | 0.000 | 75 | 11.19 | 11.21 | -0.02 |
| 35 | 0.699 | 0.699 | 0.000 | 80 | 15.11 | 15.09 | +0.02 |
| 40 | 1.027 | 1.025 | +0.002 | 85 | 20.21 | 20.21 | 0.00 |
| 45 | 1.494 | 1.498 | -0.004 | 90 | 26.78 | 26.78 | 0.00 |
| 50 | 2.146 | 2.154 | -0.008 | 95 | 35.20 | 35.24 | -0.04 |
| 55 | 3.050 | 3.069 | -0.019 | | | | |

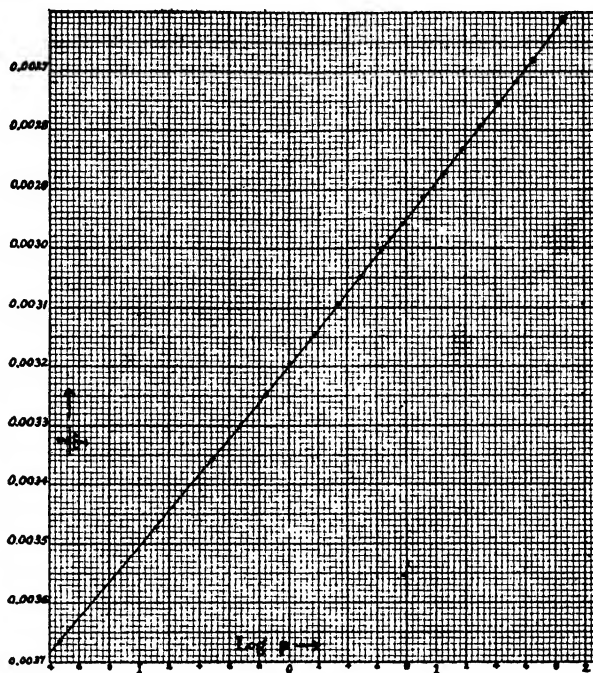
The most satisfactory results were obtained by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Through the range under consideration the points fall almost upon a straight line (see Curve 2), and by using the function $1/(T-19)$ instead of $1/T$ the plot becomes exactly a straight line within the limit of error of the experimental results. This means of course that the vapor pressure can be calculated from an equation of the form $\log p = A - B/(T - 19)$. This equation has already been proposed by Antoine.² It is essentially the thermodynamic equation without the term involving the logarithm of the absolute temperature. With the values 9.7522 and 2863.54 for A and B, respectively, Table III was computed.

Above 95° both equations yield values increasingly higher than those observed by Ramsay and Young, possibly because the vapor pressure is becoming irregular as the melting point 114° is approached. Below

¹ *J. Chem. Soc.*, 49, 453 (1886). Obtained by coating a thermometer bulb with iodine and measuring the pressure manometrically.

² *Compt. rend.*, 110, 632 (1890); 112, 284 (1891); 113, 328 (1892); 116, 170 (1893).

o° the calculated values are not widely different from those of Haber and Kerschbaum.¹



Curve 2.

TABLE III.

| Temperature centigrade. Degrees. | Vapor pressure calculated. Mm. | Vapor pressure observed. Mm. | Difference. Mm. | Temperature centigrade. Degrees. | Vapor pressure calculated. Mm. | Vapor pressure observed. Mm. | Difference. Mm. |
|--|---|---------------------------------------|--------------------|--|---|---------------------------------------|--------------------|
| 0 | 0.030 | 0.030 | 0.000 | 60 | 4.291 | 4.285 | +0.006 |
| 15 | 0.128 | 0.131 | -0.003 | 65 | 5.965 | 5.962 | +0.003 |
| 25 | 0.308 | 0.305 | +0.003 | 70 | 8.205 | 8.196 | +0.009 |
| 30 | 0.467 | 0.469 | -0.002 | 75 | 11.18 | 11.21 | -0.03 |
| 35 | 0.698 | 0.699 | -0.001 | 80 | 15.09 | 15.09 | 0.00 |
| 40 | 1.029 | 1.025 | +0.004 | 85 | 20.19 | 20.21 | -0.02 |
| 45 | 1.497 | 1.498 | -0.001 | 90 | 26.79 | 26.78 | +0.01 |
| 50 | 2.151 | 2.154 | -0.003 | 95 | 35.26 | 35.24 | +0.02 |
| 55 | 3.056 | 3.069 | -0.013 | | | | |

It is also interesting to calculate from the experimental results the molecular heat of sublimation of solid iodine by means of the Clausius equation

$$L = T \, dp/dT \, (V - V_1)$$

where L = heat of sublimation.

T = absolute temperature.

¹ *Z. Electrochem.*, 20, 296 (1914).

dp/dT = change of vapor pressure per degree of temperature, expressed in atmospheres.

V = volume of one mol of iodine vapor at T° and at vapor pressure, expressed in liters.

V_1 = volume of one mol of solid iodine at T° in liters.

The change in vapor pressure with the temperature was calculated by dividing the difference in vapor pressure in each five degree interval by five. The absolute temperature was taken as the mean of the five degree interval. The vapor pressure at this temperature was estimated from a large scale curve. V_1 is so small, compared with V , that it is neglected in the calculations. The final result is multiplied by 0.02425 to convert it from liter atmospheres to kilogram calories. The values in kilogram calories multiplied by 4.183 give the results in kilojoules.

TABLE IV.

| Temperature. Degrees. | Vapor pressure estimated. Mm. | Molecular heat of sublimation. Kilogram calories. | Molecular heat of sublimation. Kilojoules. |
|--------------------------|-------------------------------------|---|--|
| 273 + 52.5 | 2.575 | 15.0 | 62.7 |
| 273 + 57.5 | 3.630 | 14.6 | 60.9 |
| 273 + 62.5 | 5.070 | 14.8 | 62.0 |
| 273 + 67.5 | 7.000 | 14.7 | 61.6 |
| 273 + 72.5 | 9.61 | 14.9 | 62.4 |
| 273 + 77.5 | 13.03 | 14.6 | 60.9 |
| 273 + 82.5 | 17.48 | 14.7 | 61.6 |
| 273 + 87.5 | 23.33 | 14.6 | 60.9 |
| 273 + 92.5 | 30.75 | 14.6 | 61.2 |
| | | Mean, 14.7 | 61.6 |

These values agree as well as could be expected, for at 75° an error in the determination of the vapor pressure of four-hundredths of a millimeter produces an error of 1% in dp , and of 0.3% in V . In fact, the agreement of the heats of sublimation is good confirmation of the accuracy of the experimental work.

The mean value of the molecular heat of sublimation between 50° and 95° is only slightly lower than the mean between 0° and 55° as found by Baxter, Hickey and Holmes, 15.1 kilogram calories or 63 kilojoules.¹

There seems to be only a slight tendency in the heat of sublimation to diminish up to 95°, although Ramsay and Young's results between 95° and the melting point 114° do indicate a perceptible drop.²

Summary.

1. The vapor pressure of solid iodine is found to have the following values:

¹ *Loc. cit.*, 135.

² Baxter, Hickey and Holmes, *Ibid.*, 135.

| Temperature. Degrees. | Vapor pressure. Mm. | Temperature. Degrees. | Vapor pressure. Mm. |
|--------------------------|------------------------|--------------------------|------------------------|
| 50 | 2.154 | 75 | 11.21 |
| 55 | 3.069 | 80 | 15.09 |
| 60 | 4.285 | 85 | 20.21 |
| 65 | 5.962 | 90 | 26.78 |
| 70 | 8.196 | 95 | 35.24 |

2. These results together with those obtained by Baxter, Hickey and Holmes between 0° and 50° may be expressed very closely by either of the two formulas

$$\log p = -106.3930 + 46.611 \log T - 0.031677 T$$

$$\log p = 9.7522 - 2863.54/(T - 19).$$

3. The average molecular heat of sublimation of iodine at these temperatures is calculated to be 14.7 kilogram calories or 61.6 kilojoules.

A portion of the apparatus and materials used were provided through the generous assistance of the Carnegie Institution of Washington.

CAMBRIDGE, MASS.

ON FRACTIONAL DISTILLATION WITH REGULATED STILL-HEADS.

[SECOND COMMUNICATION.]

DISTILLATION OF TERNARY MIXTURES.

BY M. A. ROSANOFF, JOHN F. W. SCHULZE AND R. A. DUNPHY.

Received January 18, 1915.

On the basis of an interesting series of experiments, F. D. Brown¹ describes the distillation of mixtures through a regulated stillhead in terms of the following law, or rule: "In distillations with a stillhead maintained at a constant temperature, *the composition of the distillate is constant*, and is identical with that of the vapor evolved by a mixture whose boiling point equals the temperature of the stillhead." Sometime ago this rule was examined by Rosanoff and Bacon in connection with mixtures whose boiling-point curve passes through a maximum or a minimum,² and it was shown that in a case of this type two different distillates may be expected at certain temperatures, depending upon the composition of the liquid originally introduced into the still; but that, whichever of the two possible distillates is produced, the distillation proceeds in conformity with Brown's law, in as far as the composition of the distillate is constant, and is identical with that of the vapor evolved by a mixture whose boiling point equals the temperature of the stillhead.

But both Brown's experiments and those just mentioned dealt exclusively

¹ Brown, *J. Chem. Soc.*, 37, 59 (1880); *Ibid.*, 39, 521 (1881).

² Rosanoff and Bacon, first communication of the present series, *THIS JOURNAL*, 37, 301 (1915).

with binary mixtures. And yet the possibilities¹ that the regulated stillhead may have, especially in the industries, would mostly be in connection, not with simple binary mixtures, but with mixtures of three components or more. It seemed highly desirable, therefore, to investigate the working of the regulated stillhead in the case of a typical set of ternary mixtures, with a view to discovering the general principle involved.

The three substances chosen for the experiments were toluene, carbon tetrachloride, and ethylene bromide: their binary boiling-point curves and their ternary boiling-point surface show, as expected, neither maximum nor minimum, and therefore the case may be considered as of the simpler type. Further, the substances differ considerably in their physical properties, and thus we could expect to be able to analyze our distillates accurately by a rapid physico-chemical method.

And first the analytical method was worked out by one of us,² the work including a determination of the boiling-point surface. Then, in order to know what vapors might be expected to issue from the stillhead uncondensed, we determined³ the composition of the vapors evolved by various mixtures boiling at the temperatures: 83°, 91°, 99°, 107°, and 115°. After these preliminary steps had been taken, we were able to attack our main problem.

The powerful metallic stillhead which had been employed in the study of binary mixtures with maxima and minima in the boiling-point curves⁴ was again made use of in the present investigation. The liquids—toluene, carbon tetrachloride, and ethylene bromide—were the identical ones that Schulze had used in working out the analytical method, and a re-statement of the method of their purification is unnecessary. Each experiment consisted in fixing the temperature of the stillhead at one of the points for which we had previously determined the ternary partial pressures (composition of the vapors); then introducing into the still a mixture boiling at a somewhat higher temperature than that of the stillhead, and collecting for analysis a number of fractions sufficient to indicate the character of the distillate at every instant, and its variation—if any. Then a new run would be made, with the stillhead at the same temperature as before, but this time with a different mixture initially in the still. Thus two runs were made with the stillhead kept at 83°, and three runs at each of the remaining four temperatures. The results of the fourteen runs are reproduced in the tables below. In addition, six further runs were made

¹ Warren, *Memoirs of the American Academy*, New Series, 9, 121 (1864), and Liebig's *Ann.*, 4 (Supplementband), 51 (1865); Brown, *J. Chem. Soc.*, 37, 59 (1880); Young and Thomas, *Ibid.*, 71, 440 (1897); Lord Rayleigh, *Phil. Mag.*, [6] 4, 535 (1902); and also Young, "Fractional Distillation" (London, 1903), p. 189.

² Schulze, *THIS JOURNAL*, 36, 498 (1914).

³ Rosanoff, Schulze and Dumphy, *Ibid.*, 36, 2480 (1914).

⁴ See Rosanoff and Bacon, *Loc. cit.*, Fig. 2.

by way of a check on results that appeared somewhat doubtful; but as these additional results were practically identical with those obtained at first, their reproduction here would be superfluous.

Throughout the experiments it was important to maintain the same atmospheric pressure, *viz.*, 749.0 mm., under which the boiling points of the various ternary mixtures had been determined by Schulze;¹ for under a changed atmospheric pressure the set of liquids boiling at the temperature of the stillhead would have been different from the set previously employed in studying the composition of the ternary vapors, and consequently we should not have known what vapors to expect. The required external pressure was established, and maintained constant, with the aid of a 100 liter manostat tank connected by sufficiently wide tubing with our receiver.

The volume of liquid mixture introduced into the still amounted each time to about 400 cc. The volume of each fraction of distillate was from 15 to 20 cc., and the distillates were "analyzed" by determining their refractive indices and their densities, both at 25°. All percentages given below are by weight.

The theoretical question before us was, whether Brown's law is applicable to mixtures of more than two substances. That in part the law must hold true whatever the number of components, might be confidently expected: namely, the composition of the vapor issuing from the stillhead at any instant must quite generally be "identical with that of the vapor evolved by a liquid whose boiling point equals the temperature of the stillhead." For what issues from the stillhead, is a vapor that is saturated at the temperature of the stillhead, and therefore one that would be evolved by a liquid boiling at the temperature of the stillhead. The question whether the issuing vapor will have a constant composition is more involved. In the case of binary mixtures with neither maximum nor minimum in the boiling-point curve, there is only one mixture boiling at the temperature of the stillhead, and therefore the escaping vapor can also have but one composition. Binary mixtures with a maximum or a minimum in the boiling-point curve must still follow Brown's law and yield a vapor of constant composition, although here, as stated before, one of two different vapors may be expected at certain stillhead temperatures. The addition of a third component introduces a new degree of freedom: a given set of three substances may be mixed in an infinity of proportions to give mixtures boiling at one and the same temperature, but each mixture will evolve its own vapor. While, therefore, with the stillhead kept at the common boiling temperature of these mixtures, the escaping saturated vapor will at every instant be identical with that evolved by one of the infinity of mixtures in question, its composition will by no

¹ Schulze, *Loc. cit.*

means be determined by the stillhead temperature alone, as in the case of binary mixtures. The composition of the vapor must certainly depend also on that of the mixture originally introduced into the still. But given a certain definite mixture in the still to start with, it would not be easy to foretell whether during a single distillation (the distillation of that particular mixture) the issuing vapor would have a constant composition or not.

TABLE I.

STILLHEAD, 83°. ORIGINAL MIXTURE: 67.8% CCl_4 + 16.4% $\text{C}_6\text{H}_5\text{CH}_3$ + 15.8% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 91.4 | 5.5 | 3.1 |
| 91.4 | 5.4 | 3.2 |
| 91.4 | 5.4 | 3.2 |
| 91.5 | 5.5 | 3.0 |
| 91.5 | 5.5 | 3.0 |
| 91.5 | 5.5 | 3.0 |
| 91.5 | 5.5 | 3.0 |
| 91.4 | 5.6 | 3.0 |
| 91.4 | 5.6 | 3.0 |
| 91.4 | 5.6 | 3.0 |
| 91.4 | 5.5 | 3.1 |
| 91.4 | 5.5 | 3.1 |
| 91.4 | 5.8 | 2.8 |
| 91.4 | 5.7 | 2.9 |

TABLE II.

STILLHEAD, 83°. ORIGINAL MIXTURE: 58.4% CCl_4 + 7.7% $\text{C}_6\text{H}_5\text{CH}_3$ + 33.9% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 90.9 | 2.7 | 6.4 |
| 90.8 | 2.7 | 6.5 |
| 91.0 | 2.7 | 6.3 |
| 91.0 | 2.7 | 6.3 |
| 91.0 | 2.7 | 6.3 |
| 90.6 | 2.9 | 6.5 |
| 91.1 | 2.8 | 6.1 |
| 91.1 | 2.8 | 6.1 |
| 91.1 | 3.1 | 5.8 |
| 91.1 | 3.1 | 5.8 |
| 91.0 | 3.2 | 5.8 |
| 91.0 | 3.1 | 5.9 |
| 90.8 | 3.2 | 6.0 |

TABLE III.

STILLHEAD, 91°. ORIGINAL MIXTURE: 48.3% CCl_4 + 46.0% $\text{C}_6\text{H}_5\text{CH}_3$ + 5.7% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 78.0 | 20.9 | 1.1 |
| 78.0 | 20.9 | 1.1 |
| 78.0 | 20.9 | 1.1 |
| 78.0 | 21.1 | 0.9 |
| 78.0 | 21.2 | 0.8 |
| 78.0 | 21.1 | 0.9 |
| 78.0 | 21.2 | 0.8 |
| 78.0 | 21.4 | 0.6 |
| 77.8 | 21.4 | 0.8 |
| 77.7 | 21.8 | 0.5 |

TABLE IV.

STILLHEAD, 91°. ORIGINAL MIXTURE: 47.0% CCl_4 + 25.0% $\text{C}_6\text{H}_5\text{CH}_3$ + 28.0% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 78.7 | 13.3 | 8.0 |
| 78.7 | 13.5 | 7.8 |
| 78.7 | 13.6 | 7.7 |
| 78.7 | 13.7 | 7.6 |
| 78.5 | 14.0 | 7.5 |
| 78.7 | 14.0 | 7.3 |
| 78.7 | 14.2 | 7.1 |
| 78.7 | 14.3 | 7.0 |
| 78.7 | 14.6 | 6.7 |
| 78.5 | 14.9 | 6.6 |

TABLE V.

STILLHEAD, 91°. ORIGINAL MIXTURE: 45.0% CCl_4 + 10.2% $\text{C}_6\text{H}_5\text{CH}_3$ + 44.8% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 79.0 | 5.8 | 15.2 |
| 79.0 | 5.9 | 15.1 |
| 79.0 | 6.1 | 14.9 |
| 79.0 | 6.1 | 14.9 |
| 78.9 | 6.3 | 14.8 |
| 79.0 | 6.4 | 14.6 |
| 78.9 | 6.6 | 14.5 |
| 79.0 | 6.6 | 14.4 |
| 79.0 | 6.9 | 14.1 |
| 79.0 | 7.0 | 14.0 |
| 79.0 | 7.3 | 13.7 |
| 79.0 | 7.5 | 13.5 |

TABLE VI.

STILLHEAD, 90°. ORIGINAL MIXTURE: 28.4% CCl_4 + 54.8% $\text{C}_6\text{H}_5\text{CH}_3$ + 16.8% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 58.2 | 35.8 | 6.0 |
| 57.9 | 36.3 | 5.8 |
| 57.8 | 36.7 | 5.5 |
| 57.8 | 36.8 | 5.4 |
| 57.7 | 37.1 | 5.2 |
| 57.6 | 37.3 | 5.1 |
| 57.6 | 37.4 | 5.0 |
| 57.4 | 37.8 | 4.8 |
| 57.2 | 38.4 | 4.4 |

TABLE VII.

STILLHEAD, 99°. ORIGINAL MIXTURE: 27.2% CCl_4 + 29.3% $\text{C}_6\text{H}_5\text{CH}_3$ + 43.5% $\text{C}_2\text{H}_4\text{Br}_2$

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 62.6 | 21.0 | 16.4 |
| 62.1 | 21.6 | 16.3 |
| 62.0 | 22.0 | 16.0 |
| 61.8 | 22.4 | 15.8 |
| 61.9 | 22.8 | 15.3 |
| 61.8 | 23.7 | 14.5 |
| 61.5 | 24.3 | 14.2 |
| 61.6 | 24.7 | 13.7 |

TABLE VIII.

STILLHEAD, 99°. ORIGINAL MIXTURE: 25.0% CCl_4 + 13.9% $\text{C}_6\text{H}_5\text{CH}_3$ + 61.1% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 65.2 | 10.9 | 23.9 |
| 64.3 | 11.5 | 24.2 |
| 64.0 | 12.0 | 24.0 |
| 63.7 | 12.3 | 24.0 |
| 63.9 | 12.8 | 23.3 |
| 63.6 | 13.5 | 22.9 |
| 63.9 | 14.4 | 21.7 |
| 63.7 | 15.6 | 20.7 |

TABLE IX.

STILLHEAD, 107°. ORIGINAL MIXTURE: 10.0% CCl_4 + 70.0% $\text{C}_6\text{H}_5\text{CH}_3$ + 20.0% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 26.4 | 63.8 | 9.8 |
| 25.8 | 64.8 | 9.4 |
| 25.4 | 65.7 | 8.9 |
| 25.2 | 66.4 | 8.4 |
| 25.1 | 66.7 | 8.2 |
| 24.8 | 67.4 | 7.8 |
| 24.6 | 68.0 | 7.4 |
| 24.3 | 68.9 | 6.8 |

TABLE X.

STILLHEAD, 107°. ORIGINAL MIXTURE: 14.3% CCl_4 + 34.5% $\text{C}_6\text{H}_5\text{CH}_3$ + 51.2% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 38.8 | 33.6 | 27.6 |
| 38.4 | 34.5 | 27.1 |
| 38.0 | 35.4 | 26.6 |
| 37.7 | 36.2 | 26.1 |
| 37.2 | 37.3 | 25.5 |
| 36.8 | 38.5 | 24.7 |
| 36.2 | 40.2 | 23.6 |
| 35.6 | 42.1 | 22.3 |

TABLE XI.

STILLHEAD, 107°. ORIGINAL MIXTURE: 15.0% CCl_4 + 15.7% $\text{C}_6\text{H}_5\text{CH}_3$ + 69.3% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 45.1 | 16.9 | 38.0 |
| 45.3 | 17.3 | 37.4 |
| 45.2 | 17.8 | 37.0 |
| 44.8 | 18.7 | 36.5 |
| 44.5 | 19.6 | 35.9 |
| 44.0 | 20.7 | 35.3 |
| 43.3 | 22.4 | 34.3 |
| 42.0 | 24.2 | 33.8 |

TABLE XII.

STILLHEAD, 115°. ORIGINAL MIXTURE: 2.0% CCl_4 + 32.9% $\text{C}_6\text{H}_5\text{CH}_3$ + 64.1% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 8.1 | 47.6 | 44.3 |
| 7.7 | 48.3 | 44.0 |
| 7.2 | 49.2 | 43.6 |
| 6.6 | 50.6 | 42.8 |
| 6.0 | 51.7 | 42.3 |
| 5.2 | 53.1 | 41.7 |
| 4.5 | 53.6 | 40.9 |

TABLE XIII.

STILLHEAD, 115°. ORIGINAL MIXTURE: 4.8% CCl_4 + 26.8% $\text{C}_6\text{H}_5\text{CH}_3$ + 68.4% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 16.8 | 35.0 | 48.2 |
| 16.2 | 36.0 | 47.8 |
| 15.6 | 37.0 | 47.4 |
| 14.8 | 38.3 | 46.9 |
| 14.0 | 39.6 | 46.4 |
| 13.1 | 41.3 | 45.6 |

TABLE XIV.

STILLHEAD, 115°. ORIGINAL MIXTURE: 8.2% CCl_4 + 9.2% $\text{C}_6\text{H}_5\text{CH}_3$ + 82.6% $\text{C}_2\text{H}_4\text{Br}_2$.

Composition of distillates.

| % CCl_4 . | % $\text{C}_6\text{H}_5\text{CH}_3$. | % $\text{C}_2\text{H}_4\text{Br}_2$. |
|--------------------|---------------------------------------|---------------------------------------|
| 30.0 | 12.9 | 57.1 |
| 29.5 | 13.7 | 56.8 |
| 29.1 | 14.3 | 56.6 |
| 28.4 | 15.3 | 56.3 |
| 27.7 | 16.4 | 55.9 |
| 26.4 | 18.3 | 55.3 |

It appeared plausible to expect that a vapor of constant composition would be produced only in those cases where the ratio of the amounts of the two less volatile components is the same in the vapors as in the liquids in equilibrium with them; but that usually, even during a single distilla-

tion, the vapors issuing from the regulated stillhead would not be uniform. We thought it best, however, to submit the question to direct experiment, and our results are tabulated above.

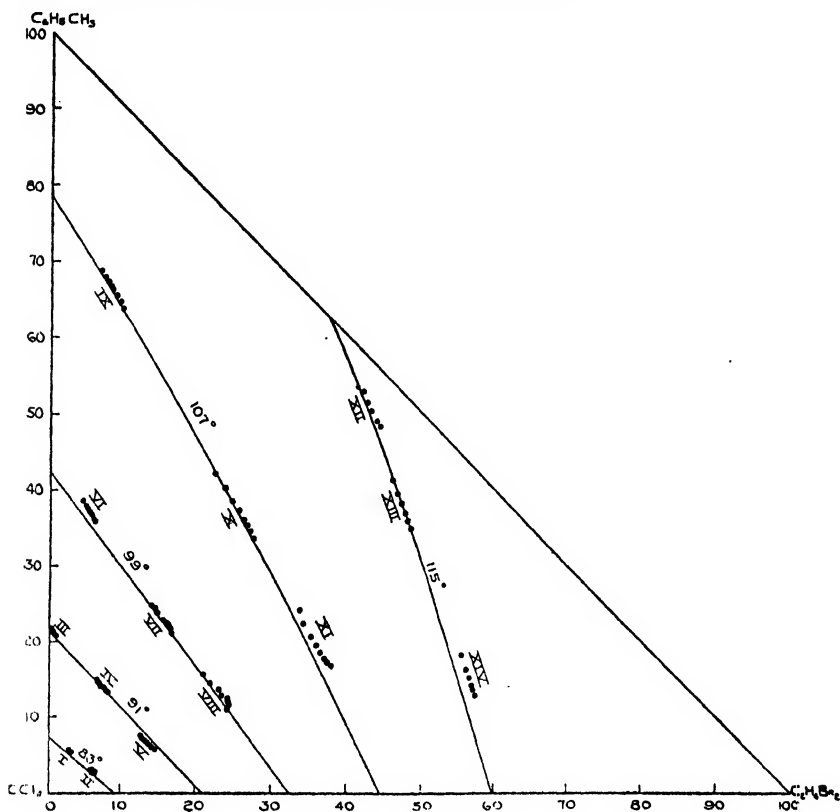


Fig. 1.

In the accompanying figure the curves represent the composition of the vapors evolved by the various liquid mixtures boiling at the stated temperatures.¹ The composition of the vapors yielded by the regulated stillhead are indicated by the several sets of points (the number near each set of points being that of the table, the results of which the set represents).

Conclusions.

Our tables and the figure answer plainly the questions under investigation.

(1) We had expected that at each stillhead temperature the distillates would have the same composition as vapors evolved by liquid mixtures boiling at the temperature of the stillhead; in other words, that the points

¹ See Rosanoff, Schulze and Dunphy, *THIS JOURNAL*, 36, 2480 (1914).

(by which we represent the composition of the distillates) would lie, in the diagram, *on the curves* which represent the composition of such vapors. As a matter of fact, the points are almost on the curves, the distance between each point and the curve to which it belongs representing in most cases only a fraction of one per cent.

(2) The different sets of points corresponding to each curve are widely separated, which shows that in the case of mixtures of three or more substances different distillates will be yielded by a regulated stillhead, if different mixtures are introduced into the still to begin with.

(3) The points of each separate set do not coincide, which shows that even during a single distillation the composition of the distillate does not remain constant.

(4) What is, however, of the greatest importance practically, is that this variation of the distillate during a single distillation is comparatively slight, as shown by the points of each set being close together. Moreover, the nearer the temperature of the stillhead is to the boiling point of the most volatile component, the more nearly constant is the composition of the distillate. Thus, as the diagram shows, for a stillhead temperature 7° above the boiling point of carbon tetrachloride, the separate points of each set can scarcely be distinguished; likewise, of course, the composition of the distillates as numerically expressed in Tables I and II is very nearly constant. *Practically the regulated stillhead can thus be used to obtain a uniform distillate from poly-component as well as from simple binary mixtures.*

(5) On the basis of the results obtained by Brown, of those of the first communication of the present series, and of those of this present communication, the working of the regulated stillhead may now be summed up in terms of the following general rule: *In distillations with a stillhead maintained at a constant temperature, the composition of the distillate is at every instant identical with that of a vapor evolved by a mixture whose boiling point equals the temperature of the stillhead. If the mixture is binary, the composition of the distillate is, in the course of a single distillation, constant. In those cases in which the binary boiling-point curve passes through a maximum or a minimum, the composition of the distillate depends on that of the mixture originally placed in the still. If the number of substances in the mixture is three or more, the composition of the distillate not only depends on that of the original mixture, but varies in the course of a single distillation. This variation, however, is moderate, and the nearer the constant temperature of the stillhead is to the boiling point of the most volatile component, the more nearly constant is the composition of the distillate. An important limitation of this rule will be demonstrated in our next communication.*

In conclusion it is a duty to recall that the cost of the apparatus used in this study was defrayed out of a grant from the Rumford Fund of the

American Academy, for which we here again cordially thank the Rumford Committee of the Academy.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH,
UNIVERSITY OF PITTSBURGH.

[CONTRIBUTION FROM THE OTHO S. A. SPRAGUE MEMORIAL INSTITUTE, LABORATORY OF CLINICAL RESEARCH, RUSH MEDICAL COLLEGE.]

A NEW METHOD OF PREPARATION AND SOME INTERESTING TRANSFORMATIONS OF COLLOIDAL MANGANESE DIOXIDE.

BY EDGAR J. WITZEMANN.

Received February 22, 1915.

Within the last few years several papers on the formation of colloidal manganese dioxide have appeared. Thus far, however, the intermediate formation of colloidal manganese dioxide in the ordinary oxidations of organic compounds with potassium permanganate has not been reported. The following paper is a report of some observations on this subject. In the course of the experiments it was found that the gelatinous form of colloidal manganese dioxide first obtained is slowly and automatically converted into a limpid colloidal solution. This transformation was studied somewhat more in detail and was found to be readily influenced (1) by the temperature at which the gel form was prepared, (2) by the concentration of the reacting solutions, (3) by the temperature to which the gel was subjected during the transformation, and (4) by the variations in the small concentrations of alkali necessary to cause the oxidation to take place rapidly.

The unusual chemical properties of manganese dioxide have for a long time occupied the attention of chemists, so that its existence as a colloid did not escape observation very long. Georgeu¹ boiled pure finely powdered Mn_2O_3 repeatedly with concentrated nitric acid and then washed the residue with water. When the wash waters were no longer acid the hydrated manganese dioxide went into solution, giving a brown liquid. He observed that the manganese dioxide is easily precipitated by the addition of very small amounts of nitric, sulfuric, or hydrochloric acids, ammonia, potassium or barium hydroxides and other compounds. Swiontkowski² found that on reducing a solution of potassium permanganate with pure neutral hydrogen peroxide a coffee-colored solution of colloidal manganese dioxide was obtained. This colloid was not obtained if the hydrogen peroxide was not neutral and was readily precipitated by the addition of very small quantities of acids and salts. Spring³ and Spring

¹ *Ann. chim. phys.*, [3] 66, 154 (1862); *Jahresberichte*, 1862, 155.

² *Ann. Chem. Pharm.*, 141, 205 (1867).

³ *Ber.*, 16, 1142 (1883).

and Boeck¹ prepared colloidal manganese dioxide by the action of hypochlorous acid on manganese hydroxide and of potassium permanganate on sodium thiosulfate. The precipitate formed dissolved in part, on washing thoroughly with water, to give dark brown solutions. The undissolved part corresponded to $\text{Mn}_3\text{O}_{12} \cdot 4\text{H}_2\text{O}$. The dissolved part, after evaporation of the water, gave $\text{Mn}_7\text{O}_{12} \cdot 4\text{H}_2\text{O}$. Spring and Boeck determined the concentrations of various electrolytes necessary to precipitate colloidal solutions of manganese dioxide and found the values to be relatively quite small. In fact it is this sensitiveness to the presence of electrolytes, no doubt, that has prevented the observation of this colloid in more instances. Aland likewise reported² that the addition of potassium permanganate to sodium thiosulfate gave no precipitate but that on the addition of sodium chloride solution manganese dioxide is precipitated. Deiss³ prepared stable colloidal manganese dioxide hydrosol direct by reducing potassium permanganate solutions with arsenious acid in the presence of sodium hydroxide. By the use of this solution he was able to observe a number of new and interesting properties of this colloid, some of which will be mentioned in more detail below. Marck⁴ reported some new observations on the formation of colloidal manganese dioxide by the reduction of potassium permanganate with hydrogen peroxide. But his results and additional data were published later in a somewhat more accessible form.⁵ Some remarkable facts about the catalytic activity of colloidal manganese dioxide are brought out in the above paper.

My own observations on the formation of colloidal manganese dioxide during organic oxidations began several years ago. On one occasion especially,⁶ while oxidizing pyruvic acid with potassium permanganate at room temperature in the presence of potassium hydroxide, the reaction mixture remained perfectly liquid after the addition of potassium permanganate, although no unchanged potassium permanganate was present as shown by the red-brown color. Gradually the mixture became more and more viscous until it set into a fairly stiff jelly. This jelly was made filterable by heating for a time.

Later⁷ the formation of colloidal manganese dioxide was observed many times in the oxidation of acrolein diethylacetal to glyceric aldehyde diethylacetal in the synthetic preparation of *dl*-glyceric aldehyde. In this oxidation 540 cc. of water were placed in a three-liter flask and 50 g.

¹ *Bull. soc. chim.*, [2] 48, 170 (1887).

² *Z. anal. Chem.*, 40, 574 (1901).

³ *Z. Chem. Ind. Koll.*, 6, 69 (1910).

⁴ *Dissertation*, Heidelberg (1907).

⁵ G. Bredig and A. Marck, "Ueber kolloides MnO_2 sol und sein Verhalten gegen H_2O_2 ," J. M. van Bemmelen, *Gedenksboek*, 1910, 342; for abstracts, cf. *Koll. Ztschr.*, 3, 333; *C. A.*, 5, 2470.

⁶ Evans and Witzemann, *THIS JOURNAL*, 34, 1099 (1912).

⁷ *Ibid.*, 36, 1912 (1914).

acrolein acetal were added. To this, 1100 cc. of an aqueous solution containing 60 g. of potassium permanganate (*i. e.*, nearly saturated at room temperature) were added from a dropping funnel at the rate of 100 cc. in five minutes. Throughout the addition the mixture was vigorously agitated in an ice bath. By the time the last of the potassium permanganate is being added the whole reaction mixture has increased in viscosity very markedly. The viscosity continues to increase gradually until in 15 to 30 minutes the entire mass has set into a dark brown jelly with a shiny mirror-like surface. This gel was so stiff that frequently the flask could be inverted for an instant without disturbing the gel. Gradually, if left undisturbed, little globules of colorless liquid appeared on the upper surface. In a short while the sides of the gel broke away from the wall of the flask and fluid filled the crevice. Presently crevices filled with liquid were formed throughout the whole mass of the gel. The quantity of liquid increased as the gel continued to contract and break up until finally the gel was submerged in the syneresis water. At about this point the syneresis water usually began to be more or less brown in color. The mixture was now placed on a steam bath and the coagulation of the very sensitive colloidal gel hastened.

When the same quantities of materials given above were used, but when the potassium permanganate was added at the rate of 100 cc. in 10 minutes, the increase in viscosity appeared some time before the addition was complete and more or less gel formation occurred toward the end of the addition, so that it was frequently difficult to agitate the reaction mixture thoroughly because of its high viscosity. In some instances coagulation took place as soon as the maximum viscosity appeared; gel formation in this case did not interfere with the process of agitation. It may be, when the potassium permanganate oxidation of acrolein acetal is carried out as originally prescribed by Wohl,¹ *i. e.*, where the permanganate is added very slowly, that the intermediate formation of colloidal manganese dioxide is almost entirely concealed. In fact, it may even be that this procedure² was originally adopted to avoid the difficulty of stirring the gel. Be that as it may, it is clear from my own experiments, that by carrying out this oxidation as described above (1) a great deal of time is saved, (2) a greater yield of the oxidation product desired is obtained, and (3) the interference offered by manganese dioxide gel to adequate agitation is avoided.

Because of the interesting and rapid transformations of this colloidal manganese dioxide, it was desirable to learn if some cheaper and more accessible organic substance would not reduce the potassium permanganate in such a way as to produce the same colloidal phenomena.

¹ *Ber.*, 31, 2394 (1898); Wohl and Neuberg, *Ber.*, 33, 3095 (1900).

² Wagner, *Ber.*, 21, 1230 (1888).

The first experiments were made with formaldehyde. 200 cc. of an aqueous solution containing 5.7 g. potassium permanganate were added to 10 cc. of 40% formaldehyde in 50 cc. of water containing a little sodium carbonate. The mixture warmed up rapidly in spite of constant agitation in the ice bath. Granular manganese dioxide was precipitated at once. The above experiment was repeated with one-half of the materials and the potassium permanganate was added very slowly. Manganese dioxide was precipitated as before. The colloidal manganese dioxide is no doubt precipitated by the potassium carbonate formed by the oxidation of the formaldehyde. The small excess of alkali added in the beginning is necessary to make the reaction take place more rapidly.

With Glucose.

(a) From the above it seemed probable that colloidal manganese dioxide would only be stable in those reaction mixtures in which the salts formed are relatively little ionized. 5 g. glucose were dissolved in 20 cc. of warm water. The mixture was now cooled in an ice bath. A few cubic centimeters of 10% sodium hydroxide were added and 100 cc. of potassium permanganate (60 g. per 100 cc.) were added through a dropping funnel in five minutes while agitating the mixture in an ice bath. The mixture rapidly became viscous and in 5 to 10 minutes set into a stiff jelly. From this point on, the transformations were entirely similar to those described above in the oxidation of acrolein acetal. Instead, however, of placing the flask containing the brownish solution, in which lumps of gel were suspended, on the hot plate it was kept at room temperature. Twenty-four hours later the brown solution had deepened in color and the lumps of gel had been changed into a thin semi-liquid gel which had separated to the bottom of the flask. In a few days more all signs of gel had disappeared and there was only a small amount of granular (perhaps crystalline) mass on the bottom of the flask. The colloid in this form was stable for months.

The limpid liquid thus obtained was dark brown, almost black, in color. In thick layers it was opaque to diffuse daylight, but in layers about $\frac{1}{16}$ inch thick it was transparent and when held over pencil marks had the effect of making them look darker in color and therefore somewhat more sharply legible. It was found that this colloid could be diluted to any extent with distilled water without causing colloidal manganese dioxide to precipitate out at any point in the dilution. The only observable effect was a gradual weakening of the brown color as the dilution progressed. This brown color persists to a very high dilution. In general the more concentrated solutions are the most stable. In one case 60 cc. of the concentrated colloid was diluted to 1.5 liters with distilled water. The solution which was too dense to be transparent while in the bottle was clear and red-brown in color when observed in a test tube. This solution was

filtered through a close thick filter (S. and S. No. 584) and only a small trace of insoluble matter remained on the filter.

It will not be necessary to enumerate all of the properties of colloidal manganese dioxide previously observed and to relate just how the above solutions showed the same characteristics. Only a few of the most striking properties will be mentioned. Deiss¹ observed that solutions of colloidal manganese dioxide dropped from a capillary tube into still water give beautiful vortex rings. If a fairly dilute solution of the above colloid is used the successive series of rings are developed very beautifully. The first ring increases to a certain size and breaks into 3 to 5 new small rings. These in turn develop until they each also break into 1 to 3 new rings. In favorable instances several more generations of rings are produced. All these rings are connected with each other by thin lines of manganese dioxide, thus giving the whole system a striking clustered or festooned appearance. This apparently little-known phenomenon was described first by Thomson and Newall² and is not limited to colloids like milk, blood, ink, etc., but is also shown by many salt solutions. Potassium permanganate of appropriate concentration gives beautiful rings. If the colloidal manganese dioxide is dropped into the solution of a salt the colloid is precipitated in the form of miniature rings. If the proper dilution of the colloid is dropped into a dilute solution of a salt (barium chloride, for example) the coagulation does not take place until the elaborate system of rings described above has been developed. It is interesting to note in this connection that the same rings and coagulated ring systems may be obtained with silver chloride, silver bromide, silver chromate, barium sulfate, etc., by dropping the proper reagents into a suitable concentration of the precipitant.

Bredig and Marck¹ studied the behavior of colloidal manganese dioxide with hydrogen peroxide very exhaustively. No attempt was made to repeat their careful quantitative experiments, but their qualitative experiments were easily duplicated with the colloid as obtained above. It was thus found, on adding hydrogen peroxide to a dilute but distinctly brown solution of the colloid, that the solution was decolorized at once but no oxygen or precipitate was formed. With somewhat stronger solutions a marked fading of the brown color took place, accompanied presently by the slow evolution of oxygen and the formation of a faint flocculent precipitate. Still stronger solutions gave a copious precipitate and oxygen very freely. Bredig and Marck explain these results by as-

suming that in dilute solutions a salt, $\text{Mn} \begin{array}{c} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{array}$, is formed which has no

¹ *Loc. cit.*

² *Proc. Roy. Soc.*, 39, 417 (1886).

catalytic activity, but in more concentrated solutions the catalytic properties of the unchanged manganese dioxide become effective. Their observations on the catalytic activation of the reduction of mercuric chloride with hydrogen peroxide by the addition of traces of colloidal manganese dioxide were also verified qualitatively.

Perhaps one of the most interesting properties of this colloid as obtained in the above and succeeding experiments is the behavior of the drops and splashings on the inside wall of the flask. These drops and thin films undergo the same syneresis described above except that here the syneresis water flows away or evaporates. The consequence is that once the cracks have begun to appear the various segments contract and curl up exactly like thin layers of drying liquid mud. If the films of colloidal solution are very thin they show after drying the metallic colors phenomena of thin films. In washing such flasks many of these scales become detached and show up brilliantly against the dark brown background of precipitated manganese dioxide. Deiss¹ considers the formation of these and other mirrors (Ag, Au, etc.) as dependent on colloidal phenomena.

(b) The preparation of colloidal manganese dioxide as described in (a) was repeated a large number of times. In these experiments additional observations on the transformation were made. It was found that on diluting the freshly prepared colloid, *i. e.*, before gelling had taken place, it could similarly be diluted to any extent without causing any precipitation of manganese dioxide. These solutions are less stable than those described in the preceding paragraphs. If other portions were diluted at different stages as the gelling progresses it was found that presently only a part of the material was dissolved. When the gelling was at its maximum nothing was dissolved and the water in which the gel was placed remains quite colorless.

Another striking indication that a molecular transformation is here taking place is shown by the marked change in color. When first prepared the colloidal solution is a rich cherry-red in color, but the red phase of the color fades out gradually as the transformation takes place, leaving a rich brown color.

From all that has gone before it is clear that we have a colloidal solution with a rather high viscosity automatically, without any marked change in temperature, being quickly converted into an insoluble gel which in turn is subsequently slowly changed into a limpid colloidal solution of the same compound. That is, there is a transformation from one molecular state in the solution into a markedly different one—a transformation which outside of colloidal chemistry might easily be spoken of as a transformation of an α -form of colloidal manganese dioxide into a β -form or *vice versa*. As a matter of fact it is quite probable that what really takes

¹ *Loc. cit.*

place is the transformation of an emulsoid form of "colloid" manganese dioxide into a suspensoid.

Examples of spontaneous isothermic transformations of the kind just described (*i. e.*, the transformation of a highly viscous colloid or gel into a colloid of low viscosity) are apparently quite rare among colloids. In some ways the transformations of molten sulfur on further heating are quite similar. But since sulfur is an isocolloid the analogy between it and the above heterogeneous colloid is only relative. Perhaps the transformation of the emulsoids of gum arabic or gelatin in water into suspensoid by the addition of definite small amounts of ethyl alcohol to the cold emulsoids is more strictly analogous.¹ It had previously been known that the addition of ethyl alcohol to these solutions would cause the gum or gelatin to separate as an amorphous or crystalline precipitate,² but Scarpa observed, if smaller concentrations of alcohol were added and the mixture kept cold throughout the addition, that a suspensoid was formed from the emulsoid, as was shown by the enormous fall in viscosity, by its electrophoric properties and by the difference in its behavior toward inorganic ions.

Our own transformation differs from that of Scarpa in that no external reagent was added in order to produce the transformation.

The spontaneous increase in the degree of dispersion of colloidal solutions of glycogen, benzopurpurin, hemoglobin, etc.,³ with increasing age of the solutions are in some respects similar, but not nearly so striking.⁴

The so-called "peptizations" of hydrogels⁵ by the addition of alkali are similar in effect to the observations described above. It seemed possible that some reaction between the sugar and the alkali might produce a difference in the chemical nature of the medium such that the gel would be liquified in it. Accordingly the glucose and alkali were allowed to stand in the aqueous solution for one week before adding the permanganate in the customary manner. The glucose solution became markedly yellow as was expected, due to characteristic chemical changes produced by the action of alkali under these conditions. When the glucose solution thus prepared was oxidized with permanganate the transformations of the colloidal manganese dioxide were just the same as those described in (a). So that it seemed clear that the changes produced in the glucose

¹ O. Scarpa, *Rend. soc. chim. ital.*, [2] 5, 375-9 (1913); *Koll. Z.*, 15, 8 (1914); *C. A.*, 8, 3522.

² P. P. v. Weimarn, *Grundzüge d. Dispersoidchemie*, p. 116; *Koll. Z.*, 2, 78 (1907).

³ Rachlmann, *Berl. klin. Wochenschr.*, 1904, No. 8; W. Biltz and Z. Gatin-Gruszevska, *Pflüger's Arch. f. d. ges. Physiol.*, 105, 115 (1904); *Compt. rend.*, 139, 507 (1904); Lemanissier, *L'etude des corps ultramicroscopiques*, Thèse, Paris (1905); R. Zsigmondy, *Z. Erkenntnis der Kolloide*, Jena 1905, p. 160.

⁴ Cf. also W. Ostwald, *Grundriss der Kolloid-Chem.*, 1909, 283, 294-7.

⁵ Lottermoser, *Z. physik. Chem.*, 60, 456 (1908); 70, 239 (1910).

by the alkali alone are not responsible for the transformations in the colloidal manganese dioxide.

L. Michaelis,¹ A. Mayer, G. Schaeffer and E. Terroine,² and v. Henri³ have observed that the size of colloidal particles varies very markedly in dye suspensions and metal and metallic sulfide sols under minute variations in the concentrations of electrolytes. And Mayer, Schaeffer and Terroine have shown that positively charged colloidal particles tend to increase in size under small concentrations of alkali, while acids cause them to diminish in size.⁴ In the case of negatively charged colloids the conditions are reversed. Now Bredig and Marck⁵ have shown that colloidal manganese dioxide is negatively charged. Further, as will be seen from the following paragraph, the transformation takes place more rapidly the more alkali there is present. So that the generalizations of Mayer, *et al.*, fit all of the observed facts and furnish a very simple explanation of the transformation of the gel into the sol. It must be stated, however, that if alkali causes this change the concentrations required to bring it about slowly, as it was observed at first, are rarely strong enough to color red litmus paper blue. It may be that the colloid protecting action of the excess glucose serves to assist the alkali effect at these low alkali concentrations, by preventing the precipitation of the manganese dioxide during the first stages of the transformation. The fact noted above, that on diluting the transformed colloidal manganese dioxide the most dilute solutions are least stable, may now be explained as being due to the fact that the alkali concentration is decreased to such an extent that condensation takes place. The rate of condensation is faster the smaller the alkali concentrations, *i. e.*, the greater the dilution.

The explanation of the first phase of the transformation of colloidal manganese dioxide involves phenomena much better known than those discussed in the preceding paragraph. There has been much work done on the changes in the viscosity of emulsoids since 1902.⁶ In general it

¹ *Deut. med. Wochschr.*, 1904, No. 2; *Virchow's Arch.*, 179, 195 (1905).

² *Compt. rend.*, 145, 918 (1907); 146, 484 (1908).

³ *Le Caoutchouc et la Guttapercha*, 1906, 510; 1908, 2404; *Compt. rend.*, 144, 431 (1907); 146, 62, 1024 (1908).

⁴ There is a tendency in discussing general properties of this kind to speak of the OH ion and H ion effect. It may be true that some colloids are not influenced by the other ion but in the case of colloidal manganese dioxide the character of the other ion is important. Colloidal manganese dioxide is precipitated by Ba(OH)₂ solutions but not by NaOH or KOH. In this case the precipitating effect of the divalent ion or the molecular Ba(OH)₂ supercedes any effect of the OH ion itself. Throughout the remainder of this paper the word alkali will be used meaning KOH or NaOH only.

⁵ *Loc. cit.*

⁶ P. von Schroeter, *Z. physik. Chem.*, 45, 75 (1903), gelatin; v. Henri, *et. al.*, *Compt. rend. soc. de Biol.*, 55, 1668 (1903) and H. Garrett, *Phil. Mag.*, [6] 6, 374 (1903)

has been shown that whereas suspensoids undergo condensations slowly so that days are required to complete observations, in emulsoids much more marked increases in viscosity take place in as many seconds or minutes. So that rapid condensation of the fresh colloidal manganese dioxide into a gel is rather to be expected.

All the properties of the colloidal manganese dioxide may therefore be explained by the simultaneous action of two forces: the one tending to condense and precipitate the colloid and the other tending to disperse the colloid. The former is a very rapid-acting process and is hastened by increase in temperature and absence of alkali. The latter is a slow-acting process in any case, but can be accelerated greatly by relatively small increases in the alkali concentration and less markedly by increase in temperature up to a certain rather low maximum. One would expect that with two interacting processes of this character quite a variety of results could be obtained by varying the conditions. This is perhaps most strikingly shown by the variations in the gel, as representing the maximum viscosity, that were observed in the experiments described below.

On the chemical side very little may be said with certainty about the changes involved here. According to Morawski and Stingl¹ the precipitated manganese dioxide has the composition $\text{KH}_3\text{Mn}_4\text{O}_{10}$ (plus or minus small amounts of impurities). The emulsoid is therefore possibly a highly hydrated form of this compound and the transformation consists in a systematic gradual squeezing out of this water until the highly dehydrated suspensoid is obtained.² The process is also probably accompanied by a decrease in the size of the molecular aggregates of manganese dioxide. Of course the truth or error of the above can only be determined by extensive further work.

It was found that the transformation of the colloid is readily affected by changes in concentration and in temperature. For instance, when 2.5 g. glucose were dissolved in 20 cc. of water and treated with a little gelatin, silicic acid and protein; A. Muller, *Ber.*, 37, 11 (1903 or 4), organic colloids; Du Pré Denning, *Diss. Heidelberg*, 1904, ferric hydroxide; G. Fano, G. Rossi, *Arch. di Fisiol.*, 1, 492, 609 (1904), gum arabic, starch and serum; G. Rossi, *Idem.*, 2, 500 (1905) and with O. Scarpa, *Idem.*, 2, 246 (1905), ferric hydroxide sol; G. Rossi, *Idem.*, 2, 272, 599 (1905), albumin; E. Cavazzani, *Idem.*, 2, 513 (1905), milk; G. Rossi, *Idem.*, 3, 171, 507 (1906), with a bibliography of 127 titles; J. Simon, *Idem.*, 4, 594 (1907); 5, 394, 402, 470, 477, 479 (1908), albumine + alcohol, etc.; P. Schidrowitz, Goldsbrough, *J. Soc. Chem. Ind.*, 28 (1909); *Koll. Z.*, 7, 241 (1910); but especially W. Biltz, *et al.*, *Z. physik. Chem.*, 73, 500 (1910); cf. W. Ostwald, *Grundriss d. Kolloid-Chem.*, 1910, 190, *et seq.*, for many other references.

¹ *J. prakt. Chem.*, [2] 18, 86 (1878); *Jahresber.*, 1878, 275; cf. also Smolka, *Sitzungsber. d. Math. Naturwissensch. Classe D. Kais. Akad. Wissensch., Wien.*, 95, II, 5-30, and Gmelin-Kraut-Friedheim, *Handbuch der Anorg. Chem.*, 3, II, 254, etc.

² Cf. Scarpa, *Loc. cit.*, for a similar effect on gelatin and gum arabic solutions produced by adding ethyl alcohol.

10% sodium hydroxide and 100 cc. of permanganate (30 g. in 1100 cc.) as in (a), the changes were typical, so far as the gel formation was concerned, but the liquefaction of the gel was only observed to a very limited extent. On the other hand, the manganese dioxide was not properly precipitated. That is, the concentration of alkali was not sufficient to disintegrate the gel rapidly.

When the above experiment was repeated by warming the glucose solution to 30°, using a little more alkali and adding the potassium permanganate as before, the temperature of the mixture rose to 45° and the mixture gelled almost instantly after the addition was completed. Coagulation in this case did not take place suddenly as it does when the concentration is double the above (Cf. Experiment 3 below). When this coagulated mass, having the appearance of thick apple butter, was allowed to stand it showed signs of liquefying and in eight days at room temperature liquefaction was complete. The limpid colloidal solution thus obtained, where complete precipitation was expected, was typical in every way.

If the same amount of glucose and water are treated with 15 cc. sodium hydroxide and then with 50 cc. potassium permanganate (60 g. in 1100 cc. water), in an ice bath, gel formation does not take place within 3 hours in the ice bath nor within 3 hours after removing it from the bath. The mixture had a somewhat higher viscosity than the transformed colloid obtained in (a), but after standing over night even this slight difference in viscosity disappeared. By increasing the concentration of the alkali, even when the permanganate concentration was doubled, the intermediate gel stage was avoided and transformation was limited to a slight loss in viscosity. This experiment showed very strikingly that the transformation is clearly dependent on the alkali concentration, whatever explanation may be accepted, and that any effect of the glucose as a colloid protector is of secondary importance in this case.

The effects of temperature were further studied as follows:

(1) The reaction was carried out as in (a) using a little more alkali. When the gel had set the mixture was placed in the refrigerator. The transformation was typical but very slow. In four days the gel had completely liquefied in the usual way.

(2) Repeated (1) but allowed the mixture to stand at room temperature. The gel completely liquefied over night.

(3) Repeated (1) except that cooling during the addition of permanganate was omitted. The temperature of the mixture went up to 45°. In about two minutes after the addition was complete the manganese dioxide set into a gel and then almost instantly coagulated completely. It was not preserved any longer.

Without giving any further details it may be said that in general, no matter what the temperature or concentration are, the viscous or gel stage tends to be formed in all cases. The rate at which this viscous stage is dispersed into the limpid stage depends primarily on the concentration of the alkali used, but also on the temperature at which the colloid is formed and also on the temperature at which it is maintained subsequently.

With Other Substances.—2.5 g. each of galactose, fructose, lactose, and sucrose were dissolved in 10 cc. of water and treated with 2 cc. 10% sodium hydroxide and with 50 cc. potassium permanganate solution (60 g. per 1100 cc.) in the ice bath. With galactose and fructose the results were practically the same as with glucose. With lactose, gelling took place only after an hour. With sucrose, a skin was formed on top of the solution before gelling took place. The gel underwent syneresis very rapidly. When the same amount of sucrose was similarly treated in the presence of 10 cc. of 10% sodium hydroxide the green color of potassium manganate was more persistent and when the red-brown color of colloidal manganese dioxide appeared, gelling and syneresis were slower. Very little, if any, of the manganese dioxide passed into solution again. Using 2.5 g. tartaric acid as the sodium salt and 2 cc. 10% sodium hydroxide as above, reduction took place with the intermediate formation of potassium manganate, and this was gradually reduced to manganese dioxide which finally set into a stiff gel. The gel did not go into solution again. Similar experiments with 3.5 g. of glycerol showed rapid reduction and coagulation to the gel stage and but little tendency to go into solution again. The above experiments were not extended in order to determine whether conditions could be found in which the results would in all ways resemble those obtained with glucose.

Hypothetical Applications.

Although the above experiments on colloidal manganese dioxide are of much interest in themselves, their interest is considerably heightened when looked at from another point of view. The enormous role of compounds of manganese in catalytic phenomena is well known. More recently, however, the role of manganese compounds in biochemical reactions has been studied rather intensively. Without attempting to review the literature (only a few recent references will be given) a few instances of its effects may be pointed out. It has been observed that small amounts of manganese compounds stimulate alcoholic fermentation as carried out in the fermentation industry.¹ The growth of fungi (*Aspergillus niger*, etc.) is markedly stimulated by the presence of manganese salts.² Many plant experiments have been made and manganese in

¹ Kayser, Marchand, *Compt. rend.*, 145, 343 (1907).

² G. Bertrand and Javillier, *Ann. inst. Pasteur*, 26, 241-9, 515-21 (1912); *Bull. soc. chim.*, 11, 212-21 (1912); *C. A.*, 6, 1916, 3444; G. Bertrand, *Compt. rend.*, 154, 381-3 (1912); *Bull. soc. chim.*, 11, 494-8 (1912); *C. A.*, 6, 3443; *Ann. inst. Pasteur*, 26, 767-77 (1912); *C. A.*, 7, 496; H. I. Waterman, *Proc. Akad. Wetenschappen*, 15, 753-64 (1913); *J. Chem. Soc.*, 104, I, 229 (1913); *C. A.*, 7, 3985.

general also has a stimulating effect on the growth of plants.¹ It is now known for instance, that the production of wheat per acre may be increased 10%, in certain soils, by sprinkling a manganese salt upon the soil. Pyrolusite (MnO_2) is one of the most effective compounds in this respect. Other experiments appear to have shown that manganese compounds stimulate metabolism in animals and increase the hemogenetic power.² And it is proposed that manganese should properly be administered therapeutically with iron in order to make the latter effective. Further, the addition of minute amounts of manganese salts increases the activity of the enzyme laccase.³ All the foregoing processes are thought to be regulated by enzymes and the manganese must therefore enter into the action of the enzyme in some way. Since enzymes are admitted to be colloidal it may be that the manganese enters into combination with the colloidal particles. These enzymes are very sensitive to slight changes in the temperature and in the chemical character of the medium in which they exist. In most cases there is no adequate chemical explanation of the variations in the activity and least of all is there any known explanation as to how minute traces of certain foreign substances can influence these reactions so markedly. Of course it is quite likely that the manganese in these cases enters into the enzymic activity in the hydrolyzed form.⁴ Now if the regulatory effect in colloidal enzymes is dependent on a variation of the total surface of the colloidal particles of the enzyme a relatively small variation would cut down or increase the catalytic activity of the enzyme enormously. If, now, something was added to the enzyme which would increase the tendency of the colloidal enzyme to remain in a greater degree of dispersion, under conditions which normally would be unfavorable to this effect, then this something would have a positive influence on the enzymatic actions under consideration. Since manganese dioxide does so definitely have this tendency to become more dispersed, it is not inconceivable that the effect of manganese compounds in biochemical reactions may be accounted for on this basis.

Summary.

1. It was found that colloidal manganese dioxide is formed not only by the use of inorganic reagents but is normally formed in the oxidation of a series of organic compounds.

¹ G. Masoni, *Stas. sper. agrar. ital.*, 44, 85-112 (1911); *C. A.*, 6, 135; Luigi Montemartini, *Staz. sper. agrar. ital.*, 44, 564-71 (1911); *C. A.*, 6, 1488; Thomassin, *Engrais*, 27, 293 (1912); *C. A.*, 6, 2130; H. Bartmann, *J. Agr. prat.*, [2] 20, 666 (1911); *C. A.*, 6, 133; G. Bertrand, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 15, 39; *C. A.*, 6, 3150; J. J. Skinner, M. X. Sullivan, *et. al.*, *U. S. Dept. Agr. Bull.* 42, *C. A.*, 8, 2442; Th. Pfeiffer, E. Blanck, *Landw. Vers. Stat.*, 77, 33-6 (1912); 83, 257-81 (1914); *C. A.*, 6, 2481; 8, 1635.

² Guido M. Piccinini, *Biochem. terap. sper.*, 2, 385-94 (1910-11); *Zentr. Biochem. Biophys.*, 13, 124; *C. A.*, 7, 369; cf. also *Arch. farm. sper.*, 10, 419-36 (1911); *Chem. Zentr.*, 1911, I, 823; *C. A.*, 5, 3075; and *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 19, 263; *C. A.*, 6, 2950.

³ Bertrand, *Compt. rend.*, 122, 1132 (1896); 124, 1032-35 (1897); *Chem. Zentr.*, 96, II, 93; 97, II, 47; *Bull. soc. chim.*, [3] 17, 619-24 (1897); *Compt. rend.*, 124, 1355 (1897); *Chem. Zentr.*, 97, II, 177; *Bull. soc. chim.*, [3] 17, 753-6 (1897); *Ann. chim. phys.*, [7] 12, 115-40; cf. also A. Bach, *Ber.*, 43, 364-70 (1910); *C. A.*, 5, 300; B. Sjollem, *Chem. Weekblad*, 6, 287-94; *C. A.*, 5, 2266; O. Dony-Henault, E. Leroy, *Bull. soc. roy. Belgique*, 1909, 387-404; *C. A.*, 4, 56.

⁴ Cf. on this N. L. Soehngen, *Centr. Bakt. Parasitenk.*, 40, II, 345-54 (1914); *C. A.*, 8, 3193.

2. That colloidal manganese dioxide is especially easily obtained by incompletely oxidizing glucose (as well as fructose and galactose) in alkaline solution with potassium permanganate.

3. That the colloidal manganese dioxide is formed under these conditions first passes into a viscous or gel stage which subsequently changes into a limpid colloidal solution.

4. That the properties of the first stage agree well with those of a typical emulsoid, while the later stage seems more characteristically a suspensoid.

5. That the transformations of the emulsoid are typical and would be normal in every way if it were not for a slower but simultaneous transformation of the emulsoid into a suspensoid, owing to the effect of the alkali in accordance with the generalizations of Mayer, *et al.*

6. That both transformations are readily affected by variations in temperature, concentration of the reacting mixture and concentration of the alkali (KOH or NaOH).

7. That low temperatures are more favorable to the formation of the colloid.

8. That the concentrated colloid described here is readily coagulated by warming.

9. Suggestions are made indicating possible relationships between the remarkable properties of manganese in biochemical reactions and the properties of colloidal manganese dioxide as described above.

CHICAGO, ILL.

A CONDUCTIVITY STUDY OF THE REACTION BETWEEN CALCIUM NITRATE AND DIPOTASSIUM PHOSPHATE IN DILUTE SOLUTION.¹

By W. A. WITHERS AND ALEX. L. FEILD.

Received January 7, 1915.

It is generally agreed that a soluble calcium salt reacts with dipotassium phosphate in the presence of an excess of ammonia to form an amorphous precipitate of tricalcium phosphate with no tendency to become crystalline on standing. When, on the other hand, ammonia is not added, there occurs a reaction in regard to which there is a great difference of opinion. The present investigation was made in order to determine the nature of the latter reaction.

Introductory.

It has been known for some time that tricalcium phosphate, when precipitated in neutral solution, has a composition which only approximates to the theoretical, due to the hydrolytic action of the solvent. This

¹ Read at the meeting of the North Carolina Section of the American Chemical Society, Raleigh, N. C., May 2, 1914.

hydrolysis has been studied by Warington¹, Georgievics,² and recently by Cameron and Hurst,³ and Cameron and Seidell.⁴ In these researches the solid tricalcium phosphate was added to a certain volume of water. Analyses were made after equilibrium conditions were reached. From a consideration of the data available, Cameron and Hurst draw the following conclusions:⁵

"From these facts it appears that no matter what compound, or mixture of compounds, containing only calcium and phosphoric acid ($\text{Ca}_3(\text{PO}_4)_m$), be placed in water there will result free phosphoric acid in the solution with separation of calcium hydroxide. The calcium hydroxide may then react to form a more basic and less soluble phosphate, or simply form a mixture with the phosphate, the solubility of which is decreased by its presence."

Furthermore, it was shown by Warington⁶ and verified by Cameron and Seidell⁶ that the decomposing action of water upon tricalcium phosphate depends upon the relative masses of the phosphate and water that are brought together.

An extensive study of equilibrium conditions in the system, lime (CaO)-phosphoric acid (P_2O_5)-water, has been made by Cameron and Seidell,⁷ and yet more fully by Cameron and Bell.⁸ The last-mentioned investigators conclude that in dilute solution, giving a neutral or nearly neutral reaction to phenolphthalein, the solid phase will be tricalcium phosphate or a solid solution of nearly the same composition; and, furthermore, that if there is a range of solution in equilibrium with tricalcium phosphate such a range would be very small.

It will now be understood that a reaction involving the formation of tricalcium phosphate will not in general be a simple one, due to the partial hydrolysis of the tricalcium phosphate to a more basic phosphate or a solid solution, containing lime as one constituent. For the sake of convenience, however, we shall consider that the tricalcium phosphate formed corresponds in composition to the theoretical, whenever equations are given for the reaction between calcium nitrate and dipotassium phosphate. Any hydrolysis which takes place can be considered subsequently and independently.

There is much disagreement among the text-books in regard to the reaction under consideration. Some give equations for the reaction which are so obviously incorrect that they will not be considered here—

¹ *J. Chem. Soc.*, 26, 983 (1873).

² *Monatsh.*, 12, 566 (1891).

³ *THIS JOURNAL*, 26, 885 (1904).

⁴ *Ibid.*, 26, 1434 (1904).

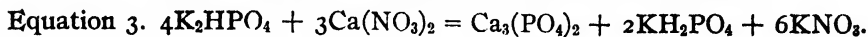
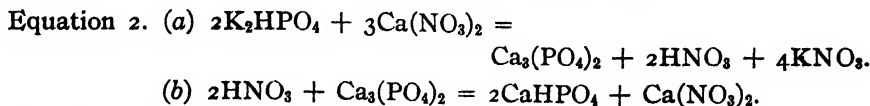
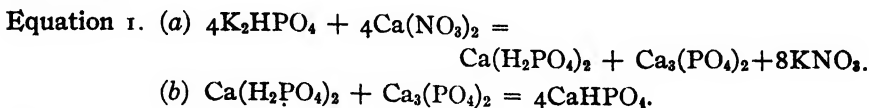
⁵ *Loc. cit.*, p. 905.

⁶ *Loc. cit.*

⁷ *THIS JOURNAL*, 27, 1503 (1905).

⁸ *Ibid.*, 27, 1512; 28, 1222 (1906).

such as the immediate formation of dicalcium phosphate. The various reactions which deserve our consideration are represented by the following equations:



The second step in Equation 1 is usually considered to take place very slowly, but more quickly upon acidifying.¹

Equation 1 is given by Remsen.²

Similarly the second step in Equation 2 would occur only after long standing. Lang and Kaufman³ give an equation analogous to (2) as being that generally accepted by texts as representing the reaction between silver nitrate and disodium orthophosphate.

The present investigation makes use of conductivity measurements to determine what reaction, or reactions, actually take place when calcium nitrate is added in increasing quantities to a given quantity of dipotassium phosphate. The volume is kept constant. The concentration employed throughout the investigation is 1 g. of K_2HPO_4 per liter, to which calcium nitrate is added in quantities up to 500 mg. nitrogen, as calcium nitrate, per liter. Whenever solutions of phosphoric acid or monopotassium phosphate are used, their concentration is equivalent to 0.5455 g. PO_4 per liter, which is the amount of PO_4 present in 1 g. of dipotassium phosphate.

After deciding which equation correctly expresses the reaction, this conclusion is verified by determinations of the composition of the liquid phase at various stages of the reaction. The method of conductivity titrations is employed for these determinations.

Method and Apparatus.

The solutions of calcium nitrate used were standardized by precipitating as calcium oxalate and titrating the precipitate with 0.1*N* permanganate, standardized by means of pure ferrous ammonium sulfate. The phosphoric acid and phosphate solutions were analyzed by precipitating with magnesia mixture, igniting, and weighing as magnesium pyrophosphate. Duplicate analyses agreed very closely.

¹ Ostwald, "Principles of Inorganic Chemistry" (1902), p. 522.

² Remsen, "Chemistry" (1890), p. 538.

³ THIS JOURNAL, 27, 1515 (1905).

The solution of potassium hydroxide contained a small quantity of carbonate, and was carefully protected from the atmosphere. It was standardized by a conductivity titration with hydrochloric acid, which, in turn, had been analyzed by weighing as silver chloride. The nitric acid solution was similarly standardized by the conductivity method against the standardized potassium hydroxide solution. Both of these solutions had a normality of 0.0574. 10 cc. of either acid or base reacted with 100 cc. of the phosphate solutions, according to equations which will be given later.

The same cell was used in all measurements of conductivity, and was of the "dipping electrode" type for dilute solutions as furnished by Eimer and Amend. It was standardized by means of 0.005 *N* potassium chloride solution, and showed a cell constant of 0.1222. Corrections were made in all cases for the conductivity of the distilled water from which the solutions were made up. Measurements were made according to the usual method of Kohlrausch. The slide-wire, furnished by Fritz Kohler, was carefully calibrated, and the resistances used had a guaranteed accuracy of a few tenths of one per cent. The electrically heated thermostat was operated throughout the investigation at 30°, and was controlled by a vapor-pressure thermoregulator, previously described by one of us,¹ which kept the bath constant within 0.01°.

When a single conductivity measurement was to be made upon a solution, a portion of the solution was removed and placed in a thin-walled test tube immersed in the bath. The conductivity cell was then dipped into the test tube, and, after temperature equilibrium was reached, the bridge reading was taken.

When a conductivity titration involving a number of measurements was made, 100 cc. of the unknown solution, diluted with distilled water to 200 cc., was placed in a spherical short-necked flask supplied with a three-hole stopper. Through this passed a stirring rod, the conductivity cell, and the tip of a buret containing the reagent which was added in the desired amount. After each addition of reagent from the buret the contents of the flask were stirred and allowed to attain the temperature of the bath before bridge readings were taken. In addition the cell was raised and lowered several times during this interval so as to allow the solution between the electrodes to mix with the surrounding solution.

The general principles underlying this and similar methods of physico-chemical volumetry have been discussed in detail by P. Dutoit.² The apparatus used by him is essentially the same as the one herein described, except that we use a different form of cell, which cannot be affected by such operations as stirring, and addition of reagent.

¹ THIS JOURNAL, 36, 72 (1914).

² Bull. soc. chim., 7 (1910).

Part I. Experimental.

Conductivity Measurements.—Varying quantities of a solution of calcium nitrate were added to a solution of dipotassium phosphate of constant composition (1 g. per liter). Three series of measurements were made on these mixtures, as follows: 1. Immediately after mixing; 2. At the end of 24 hrs.; 3. At the end of 48 hrs. During the entire time the solutions were kept in stoppered bottles at a temperature of 30°, and were repeatedly shaken, especially before conductivity measurements were made.

The results are given in Table I. Values are expressed in $\text{ohms}^{-1} \text{cm}^2$.

TABLE I.

1 g. K_2HPO_4 per liter.

| Solution number. | Mg. N as $\text{Ca}(\text{NO}_3)_2$ per liter. | Specific conductivity. | | |
|------------------|--|------------------------|---------------------|---------------------|
| | | 1. $t = 0$ hrs. | 2. $t = 24$ hrs. | 3. $t = 48$ hrs. |
| 1..... | 0 | 0.001425 | 0.001425 | 0.001425 |
| 2..... | 2.5 | 0.001437 | 0.001435 | |
| 3..... | 5.0 | 0.001447 | 0.001448 | 0.001450 |
| 4..... | 7.5 | 0.001471 | 0.001435 | |
| 5..... | 8.75 | 0.001451 | 0.001426 | |
| 6..... | 10.0 | 0.001464 | 0.001435 | 0.001435 |
| 7..... | 25.0 | 0.001496 | 0.001446 | 0.001446 |
| 8..... | 50.0 | 0.001574 | 0.001472 | 0.001468 |
| 9..... | 100.0 | 0.001750 | 0.001563 | 0.001551 |
| 10..... | 120.0 | 0.001806 | 0.001620 | |
| 11..... | 150.0 | 0.002019 | 0.001856 | 0.001856 |
| 12..... | 200.0 | 0.002261 | 0.002247 | 0.002251 |
| 13..... | 300.0 | 0.003032 | 0.003022 | 0.003026 |
| 14..... | 350.0 | 0.003402 | 0.003396 | 0.003404 |
| 15..... | 500.0 | 0.004517 | 0.004521 | 0.004521 |

Equilibrium conditions seem to have been practically reached at the end of 24 hrs., but the values for the 48 hr. period will be considered as representing more nearly such a condition. There is, however, very little difference between the two sets of values—less than 1% in all cases. As a matter of fact both of these sets of values are approximately attained after the lapse of several hours.

Fig. 1 shows graphically the conductivity values for the varying additions of calcium nitrate—the dotted curve representing initial conditions (immediately after mixing), while the continuous curve represents values at the end of 48 hrs. In Fig. 2 is represented, on a larger scale, the first portion of the two curves.

The Conductivity Curve—Time 48 hrs.—We will first confine our attention to the continuous curve representing conditions at the end of 48 hrs. It will be observed (Fig. 1) that there is a decided break in the curve at a point corresponding to the addition of about 120 mg. N as calcium nitrate. In accordance with the well-known principle discussed

by Dutoit¹ and by Miolatti and Pizzighelli,² such a break undoubtedly represents the completion of some reaction. Now of the equations

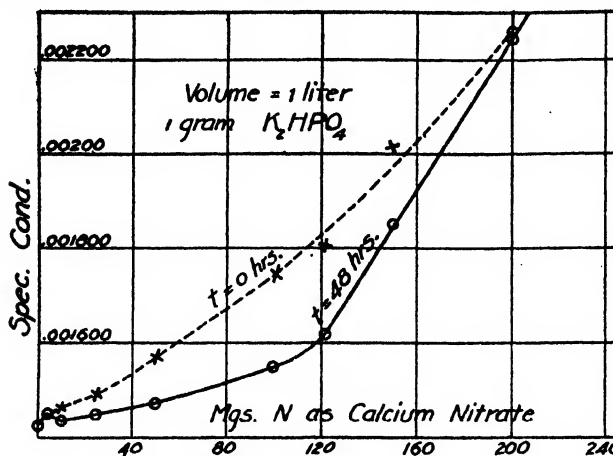


Fig. 1.

given above for the reaction between calcium nitrate and dipotassium phosphate, the only one which requires these particular proportions (120 mg. N to 1 g. of K_2HPO_4) is Equation 3. Both Equations 1 and 2 require 160 mg. N as calcium nitrate for complete reaction with 1 g. of K_2HPO_4 .

All evidence to be presented later in this article appears to strengthen this conclusion. Although several of the leading texts state that dicalcium phosphate is a final product of the reaction, we have not observed any formation of this salt in solutions which have stood several months. If such a formation occurs, it progresses with extreme slowness.

It will be noticed that the first portion of the curve shows rather striking irregularities. The maximum which occurs at a point corresponding to the addition of 5 mg. N evidently represents the beginning of the formation of a precipitate. The solutions containing quantities of calcium nitrate up to this amount remained perfectly clear on standing. That small part of the curve representing the addition of from 5 to 10 mg. N shows the occurrence of some reaction whose exact nature is rather doubtful. We can say

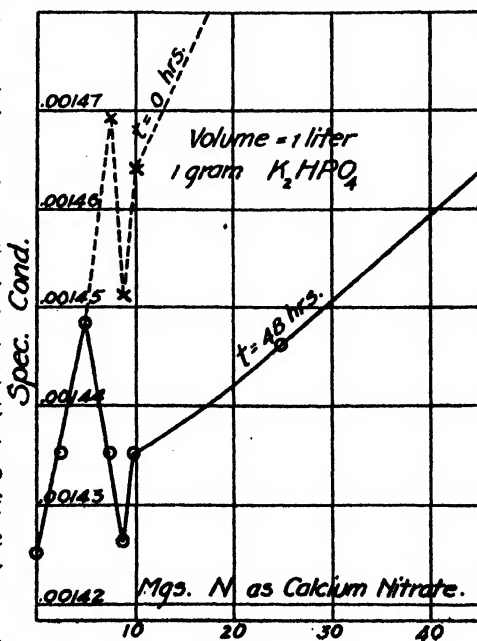


Fig. 2.

¹ Loc. cit.

² J. prakt. chem., 77, 417; C. A., 2,

with certainty, however, that the portion between 10 and 120 mg. N represents a reaction which, neglecting any hydrolysis of the tricalcium phosphate, can be represented by Equation 3. Further addition of calcium nitrate gives a curve which is practically a straight line, showing that this excess of calcium nitrate gives rise to no definite reaction with precipitate or solution. The results given later in this article indicate that an excess of calcium nitrate decreases slightly the amount of PO_4 present in solution, which effect may be looked upon as a further precipitation of tricalcium phosphate, or a lowering of the solubility of the same. Moreover, under the conditions of our experiment, tricalcium phosphate appears to dissolve as the dicalcium salt.

Conductivity Curve—Time 0 hrs.—In making conductivity measurements upon freshly mixed solutions it was noticed from the values obtained that the solutions were undergoing, in many cases, a comparatively rapid change. This change in conductivity occurred only for a short while after mixing, and was always toward a lower value.

An attempt was made, therefore, to make a series of measurements as soon as possible after mixing in order to obtain the maximum value. The results are those given in Table I, Column 1, and are represented graphically by the dotted curve in Figs. 1 and 2. Both solutions were brought to the temperature of the bath independently, and then mixed rapidly so as to avoid heat loss. In this way bridge readings could be taken within one or two minutes after mixing. Nevertheless, this set of readings can not be considered as accurate as those obtained later upon the same mixed solutions. The points as plotted lie on a fairly smooth curve. It intersects the curve representing conditions at the end of 48 hrs. at a point corresponding to about 200 mg. N as calcium nitrate, and from that point onward practically coincides with it. On account of the difficulty in obtaining the readings, it is impossible to say whether there is any break along this portion of the dotted curve. There is, however, a well defined maximum at a point corresponding to 7.5 mg. N, which is probably analogous in its significance to that present in the lower curve, and marks the point at which the precipitation reaction begins.

A special study of one solution mixture was made in order to determine, if possible, something concerning the rapidity and progress of the change in conductivity mentioned above, which is doubtless due to some chemical reaction. A solution containing the usual quantity of dipotassium phosphate (1 g. per liter), to which 80 mg. N as calcium nitrate had been added, was selected for this experiment. The change seemed to be particularly noticeable at such a concentration of the latter salt.

Conductivity values, determined at various intervals, are given in Table II.

TABLE II.

| 80 mg. N as calcium nitrate to 1 g. K_2HPO_4 . Volume, 1 liter. | | | |
|---|------------------------|------------|------------------------|
| Time. Min. | Specific conductivity. | Time. Min. | Specific conductivity. |
| 0 | 0.001667 | 11 | 0.001623 |
| 1 | 0.001667 | 13 | 0.001555 |
| 3 | 0.001662 | 15 | 0.001532 |
| 5 | 0.001662 | 17 | 0.001546 |
| 7 | 0.001662 | 19 | 0.001546 |
| 9 | 0.001653 | 23 | 0.001546 |

This experiment was repeated several times. The initial and final values were identical in each case; and, after the major change in conductivity began, the change was completed in practically the same time. In some cases, however, a longer time elapsed than that shown in Table II before the drop in conductivity began; in no case did this occur before the lapse of seven minutes after mixing. It seems then that there is some unstable compound present which changes over into another form comparatively rapidly when once started. All these solutions were stirred vigorously and continuously, so that temperature conditions and concentration was constant throughout the solution under observation.

Since an appreciable time elapsed before this drop in conductivity occurred, an attempt was made to separate the liquid phase from the precipitate before the change occurred. Such was accomplished by filtering by suction through a hardened filter on a Buchner funnel. The filtrate was perfectly clear. After standing for about thirty minutes this filtrate became cloudy from the formation of a precipitate, probably of tricalcium phosphate. This shows that the observed change in conductivity is at least partly caused by a precipitation reaction, and not entirely by the action of the supernatant solution upon the precipitated tricalcium phosphate, such as would accompany the formation of dicalcium phosphate either by hydrolysis or by a reaction similar to that indicated by Equation 1b.

While there is no direct evidence in support of the conclusion, it appears probable that the phenomenon described may be due to the temporary formation of monocalcium phosphate along with the tricalcium phosphate, in accordance with Equation 1a given above. This salt is, as shown by Cameron and Seidell,¹ unstable in dilute solution, being easily hydrolyzed. This monocalcium phosphate, temporarily formed, would be converted into tricalcium phosphate in accordance with the equation,



If we combine Equations 1a and 4 we obtain Equation 3, which, as has been shown, represents conditions after equilibrium is reached.

¹ *Loc. cit.*

Discussion of Results.—All solutions of dipotassium phosphate to which calcium nitrate had been added with formation of a precipitate showed an acid reaction to phenolphthalein and to litmus, due to the presence of the monopotassium phosphate formed according to Equation 3. Congo red showed the presence of free acid in no case, nor did the conductivity titrations performed later give any indication of the presence of free acid, either nitric or phosphoric. It seems that the absence of free acid could have been predicted from purely chemical considerations. Free nitric acid acts upon dipotassium phosphate in dilute solution with the formation of monopotassium phosphate and potassium nitrate, while phosphoric acid gives only monopotassium phosphate. In either case, any acid formed by the progress of the imaginary reaction would finally convert all of the dipotassium phosphate into the more acid salt. Furthermore, monopotassium phosphate does not form a precipitate even with an excess of calcium nitrate.

Part 2. Experimental.

The liquid phase in contact with the phosphate precipitates in the various mixtures evidently contains varying quantities of dipotassium phosphate and monopotassium phosphate, together with potassium nitrate, and if added to the mixture in excess, calcium nitrate also. A knowledge of the relative proportions of mono- and dipotassium phosphate present in the various mixtures would, if obtained, lead to a confirmation of one of the several reactions given previously in this discussion. It might be mentioned at this point that the evidence obtained from such analytical results confirms the existence of the reaction expressed by Equation 3 as representing conditions at the end of 48 hrs. On account of the short duration and instability of the first step in the interaction of the two salts, for which we suggest Equation 1a, no analytical results could be obtained to prove its existence with certainty.

In order to investigate with the greatest possible accuracy the composition of the liquid phase, we have made use of some of the principles found in the work of Berthelot¹ on the basicity of phosphoric acid, and in the work of Thiel and Roemer² on the same subject.

Berthelot found that, when a solution of potassium or sodium hydroxide is added in increasing amounts to a given quantity of dilute phosphoric acid, the conductivity decreases regularly until sufficient alkali is added to form the primary salt. Here there is a sharp break in the curve, which proceeds regularly with increasing conductivity values until sufficient alkali is added to form the secondary salt. At this point there was a decided change in direction of the curve again, although not so sharply defined as the first break. There was no break observed corresponding

¹ *Compt. rend.*, 113, 851 (1891).

² *Z. physik. Chem.*, 63, 711 (1908).

to the formation of the normal salt. Thiel and Roemer¹ observed that the position of these breaks in the curve depended to some extent on the concentrations employed, and that, for very dilute solutions approached most nearly to the theoretical value. We have found that this method may be used for quantitatively determining the amount of phosphoric acid and dihydrogen phosphate present in a dilute solution. Furthermore, we have originated a somewhat similar method for determining the amount of dipotassium phosphate present, *e. g.*, by the addition of increasing quantities of nitric acid to the phosphate solution. There is a very sharp break corresponding to the transformation of the dipotassium into the monopotassium salt. Dutoit¹ gives similar curves, obtained by adding to a phosphate solution uranyl nitrate according to the well-known analytical practice.

Conductivity Titration of Phosphoric Acid.—This proceeds according to the equation:

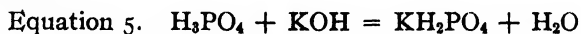


Fig. 3 shows the character of the curve obtained. At this dilution it is very similar to the ordinary neutralization curve of a strong acid. This is given merely for the sake of completeness, since no free acid was observed in the course of the analyses.

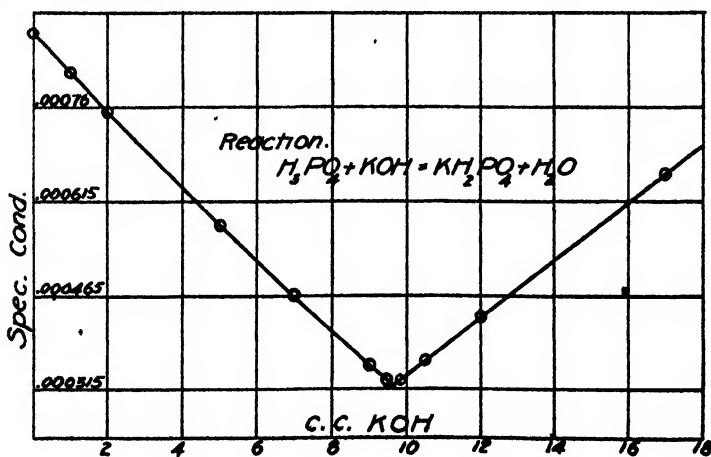


Fig. 3.

Conductivity Titration of Dihydrogen Phosphate.—This takes place according to the equation,

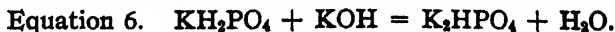


Fig. 4 shows the character of the conductivity curve obtained. While Berthelot¹ and Thiel and Roemer¹ did observe a more or less noticeable break at this point, they did not suggest that such was decided enough

¹ *Loc. cit.*

for use in a quantitative determination of dihydrogen phosphate. Since the present investigation is concerned with concentrations which vary within comparatively narrow limits, it has been found practical to use this break for the accurate determination of this form of phosphoric acid when present in dilute solutions, such as heretofore described.

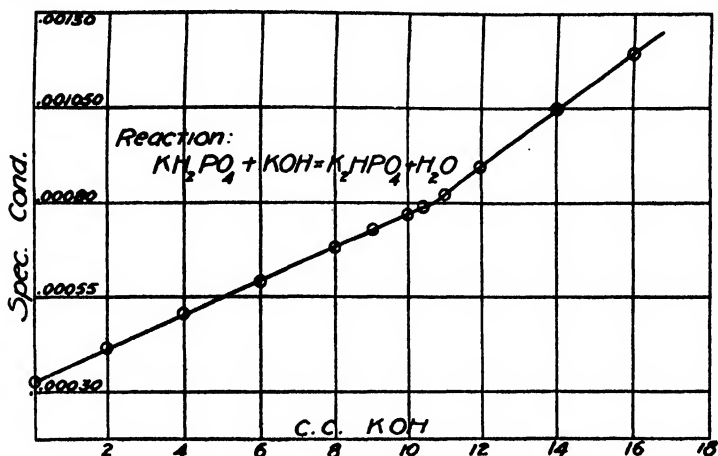
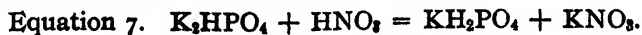


Fig. 4.

It was necessary, however, to apply corrections which were directly proportional to the total phosphate present in solution. The break was found to occur in all cases at a point beyond the theoretical addition of alkali. The excess of monopotassium phosphate, calculated from the curve, amounted to 11.8% of the total phosphate present in the solution, both being measured as grams of PO_4 per liter. In order to verify the existence of this break beyond the theoretical point indicating the completion of Equation 6, potassium hydroxide was added in varying amounts to a similar quantity of dipotassium phosphate. A break in the conductivity curve, identical in its nature, was observed when alkali corresponding to 11.8% of the total phosphate had been added. This proof was regarded as conclusive.

Conductivity Titration of Monohydrogen Phosphate.—This is possible on account of the fact that the equation,



goes to completion in dilute solution, or practically so. The conductivity curve is shown in Fig. 5. In contrast to the titration of dihydrogen phosphate, the present procedure requires a smaller amount of acid than the theoretical, the difference between the observed and calculated quantities being again proportional to the total amount of phosphate in the solution. This correction of the observed value for monohydrogen

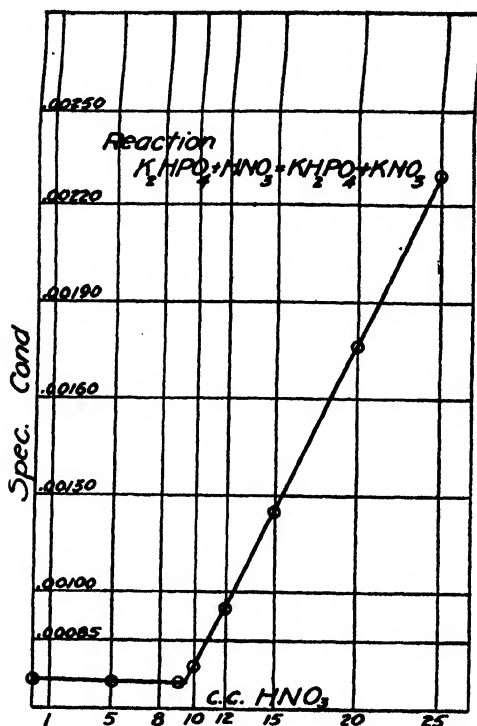


Fig. 5.

phosphate under our experimental conditions amounted to 5.0% of the total phosphate present.

Results of Conductivity Titrations.—It has been assumed that the breaks in the conductivity curves obtained by adding either potassium hydroxide or nitric acid are not sufficiently affected by the amounts of potassium nitrate, initially present in the mixtures, to appreciably alter the results obtained. In those cases where calcium nitrate had been added in excess, it was not possible to determine the amount of dihydrogen phosphate present without the formation of a precipitate of tricalcium phosphate at the point where enough potassium hydroxide had been added to render the solution alkaline. It is possible, however, that even in such cases there is a break

corresponding to the amount of dihydrogen phosphate present.

Since in all solutions investigated the total phosphate was made up only of mono- and dihydrogen phosphate, the total phosphate was first approximately determined as being equal to the sum of the uncorrected values of the two latter forms. Using this value of total phosphate for calculating the magnitude of the corrections to be applied, as described above, new values were obtained for the amounts of mono- and dihydrogen phosphate. This furnished a more nearly correct value for total phosphate than the one first used. Three successive approximations were sufficient.

Determinations, by means of the methods and apparatus described, of H_2PO_4 , HPO_4 , and total PO_4 were made upon six solutions representing various points in the reaction between calcium nitrate and dipotassium phosphate. The results are given in Table III, together with the theoretical values which should obtain if we consider that Equation 3 represents the reaction which occurs. The results are represented graphically in Fig. 6. The dotted lines in this figure represent the theoretical values. All values in the table and figure represent percentage of original PO_4 (0.5455 g. per liter).

TABLE III.—COMPOSITION OF LIQUID PHASE.

Volume, 1 liter; 1 g. of K_2HPO_4 initially.

| Mg. N as $Ca(NO_3)_2$ added. | PO_4 as HPO_4 . | | PO_4 as H_2PO_4 . | | Total PO_4 . | |
|------------------------------------|---------------------|-------|-----------------------|-------|----------------|-------|
| | Found. | Calc. | Found. | Calc. | Found. | Calc. |
| 20 | 8.78 | 8.37 | 0.82 | 0.82 | 9.60 | 9.19 |
| 50 | 6.04 | 5.91 | 2.26 | 2.04 | 8.30 | 7.95 |
| 80 | 3.85 | 3.44 | 3.66 | 3.28 | 7.51 | 6.72 |
| 100 | 2.53 | 1.82 | 4.28 | 4.09 | 6.81 | 5.91 |
| 120 | 1.58 | 0.00 | 5.14 | 5.00 | 6.72 | 5.00 |
| 150 | 1.37 | 0.00 | .. | 5.00 | .. | 5.00 |

Discussion of Results.—The results of the conductivity titrations, given in Table III and shown graphically in Fig. 6, bring to light some interesting points. In the first place, there is close agreement between

the observed and theoretical values for dihydrogen phosphate throughout the range of solution mixtures investigated. The observed values, however, for monohydrogen phosphate and total phosphate exceed the theoretical by amounts which increase with increasing quantities of

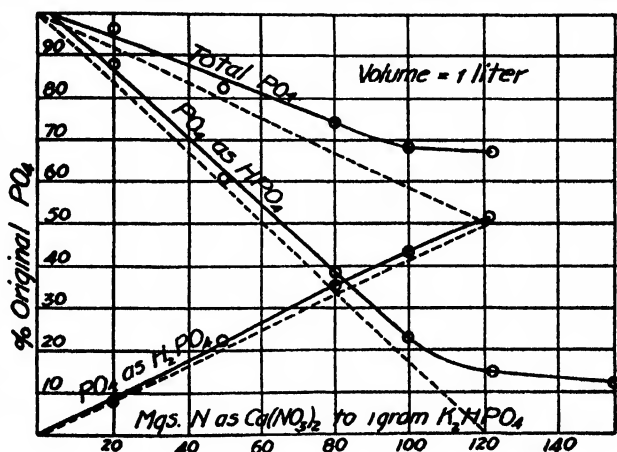


Fig. 6.

calcium nitrate, up to a point corresponding to the completion of the reaction expressed by Equation 3. Beyond this point further addition of calcium nitrate diminishes slightly the amount of monohydrogen phosphate present.

These data indicate that the principal reaction to be considered is, as has been proposed previously in this article, expressed by Equation 3. Furthermore, the tricalcium phosphate formed in accordance with this equation appears to be so hydrolyzed that a portion dissolves as monohydrogen phosphate, the resulting calcium oxide probably forming a solid solution with the remainder of the unhydrolyzed tricalcium phosphate. There are no indications to show that dihydrogen phosphate is formed by the hydrolysis of tricalcium phosphate under the conditions of these experiments. An examination of Table III will show that the extent of this hydrolysis, which is measured by the excess of the observed value of monohydrogen phosphate above the theoretical, increases with increas-

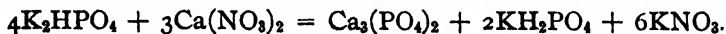
ing amounts of calcium nitrate, and is approximately proportional to the amount of the latter. This may be considered as due to the progressive formation of dihydrogen phosphate in accordance with Equation 3, and the resulting increase in the hydrogen ion concentration.

Finally we can conclude that an excess of calcium nitrate diminishes slightly the hydrolysis of tricalcium phosphate.

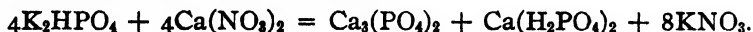
Summary.

1. A conductivity study of the reactions between calcium nitrate and dipotassium phosphate in dilute solution has been made. A constant concentration of dipotassium phosphate (0.5455 g. PO_4 per liter) has been employed, with amounts of calcium nitrate varying from 0 to 500 mg. N as calcium nitrate per liter.

2. From the occurrence of a break in the conductivity curve representing the addition of 120 mg. N as calcium nitrate per liter, the conclusion is drawn that the reaction which obtains at the end of 48 hrs. (for practical purposes, at the end of one or two hours) can be represented by the equation

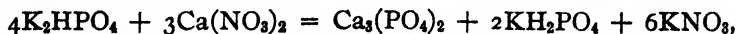


3. Evidence is presented to show that for a short while after mixing there occurs some reaction, probably



This is an unstable condition, however, and persists for a short while only (about seven minutes in the case investigated). After this short interval has elapsed, there occurs a reaction which is characterized by further precipitation of tricalcium phosphate and which results in a condition shown by the equation immediately preceding. This reaction establishes a stable condition. It proceeds very rapidly at first, more slowly finally. The unstable condition is never reached when an excess of calcium nitrate is added, or else persists for an exceedingly short time. In this case the stable condition is reached immediately.

4. In order to further verify the occurrence of the equation,



the liquid phase of a number of solution mixtures was analyzed at the end of 48 hrs. by means of a method of conductivity titration. These mixtures represented various steps in the progress of the reaction. A comparison of the observed values for mono- and dihydrogen phosphate and total phosphate with the theoretical values was then made.

5. The amount of dihydrogen phosphate in the liquid phase was determined by means of the break in the conductivity curve obtained on adding increasing amounts of dilute potassium hydroxide solution. While the occurrence of this break has been recorded by previous investigators, its location does not seem to have been hitherto utilized for a quantitative analysis of an unknown solution.

The amount of monohydrogen phosphate in the liquid phase was determined by means of a similar break obtained on adding increasing amounts of dilute nitric acid. In this case both the principle involved and its application to physico-chemical volumetry are given here for the first time.

6. The results of the conductivity titrations further verify the equation given in paragraph 2 above.

7. Furthermore, the deviation of the observed values of monohydrogen phosphate from the theoretical shows that the precipitated tricalcium phosphate undergoes partial hydrolysis, in such a way as to appear in the liquid phase as monohydrogen phosphate.

8. The extent of this hydrolysis is roughly proportional to the concentration of the dihydrogen phosphate present, and is slightly diminished by excess of calcium nitrate.

NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION,
WEST RALEIGH.

THE BEHAVIOR OF CERTAIN HYDRAZINE SALTS ON DECOMPOSITION BY HEAT.¹

By J. W. TURRENTINE.

Received December 14, 1914.

In 1899 Sebanejeff² described a method for the preparation of hydronitric acid depending upon the action of nitric acid on hydrazine sulfate. It was observed that when hydrazine mononitrate was treated with concentrated sulfuric acid at ordinary temperature, nitric oxide was evolved, a reaction which did not occur at -15° . On heating with dilute sulfuric acid, hydronitric acid was produced and was given off.

The hydrazine dinitrate, which proved to be much less stable than the corresponding monocompound, was decomposed under three sets of conditions and its decomposition products were studied—(1) at 80° to 85° ; (2) on a water bath, with a limiting temperature of 100° ; (3) at ordinary temperatures over sulfuric acid.

On warming this compound to 80 to 85° , this author found that the nitrate decomposed and yielded the volatile products, hydronitric acid, nitric acid, nitrogen and water, and the nonvolatile products, the neutral mononitrate and ammonium nitrate. Upon heating on the water bath, at 100° , the decomposition of the dinitrate occurred very much as it did at the temperature of 80 – 85° , except that the decomposition was more complete, yielding a residue containing only ammonium nitrate.

When the hydrazine dinitrate was allowed to stand at ordinary temperature in a desiccator over sulfuric acid, there occurred a continuous evolu-

¹ A chapter from the thesis submitted by the author to the Faculty of Cornell University, May 1908, for the degree of Doctor of Philosophy.

² *Z. anorg. Chem.*, 20, 21 (1899).

tion of hydronitric acid accompanied by a disintegration of the crystals. The residual powder on analysis proved to be ammonium nitrate and hydrazine mononitrate.

Within the last few years¹ it has been shown in this laboratory that hydronitric acid may be obtained by the action of a number of different oxidizing agents in acid solution on hydrazine sulfate. With a view to determining whether hydrazine salts of acids, the action of whose other salts upon hydrazine sulfate have been previously studied, would yield hydronitric acid as one of their decomposition products, the investigation to be described in the present chapter was undertaken. The results obtained are classified under the following headings:

Decomposition of: (1) hydrazine monochlorate; (2) hydrazine dichlorate; (3) hydrazine monoperchlorate; (4) hydrazine diperchlorate; (5) hydrazine monosulfate; (6) hydrazine disulfate.

Decomposition in Solution.

The apparatus used for the decomposition of solutions consisted of a 200 cc. distilling flask and an ordinary condenser, the lower end of which was connected by means of a long-stemmed adapter with a receiver containing a few cubic centimeters of distilled water for the absorption of the hydronitric acid.

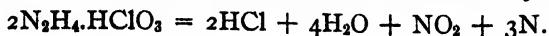
The procedure followed consisted in the careful distillation of a measured volume of the solution under consideration and in the cautious heating of the residue (in case any was obtained) until no further action was observed to take place. The distillate was divided into several fractions, each of which was treated with three drops of a 5% solution of ferric chloride. From the intensity of the color produced some idea was obtained of the relative amounts of the acid present.

Decomposition of a Solution of Hydrazine Monochlorate.—Salvadori,² anticipating us in our work on the chlorates and perchlorates, while the work was still in progress in this laboratory published in complete form a description of the methods of preparation and properties of the monochlorate and the monoperchlorate of hydrazine. His interest in, and study of these compounds, however, was in connection with their explosibility. He found that the chlorate crystallizes in unstable, hygroscopic, laminated crystals and, when placed in hydrochloric acid, evolves chlorine. In concentrated sulfuric acid it explodes; if the sulfuric acid has been warmed to 80° explosion occurs with a loud report and a terrific local effect. A study of the decomposition products formed when the decomposition occurs explosively led the author to the conclusion that

¹ Browne, *THIS JOURNAL*, 27, 551 (1905); *Ber.*, 38, 1825 (1905); Browne and Shetterly, *THIS JOURNAL*, 29, 1305 (1907); 30, 53 (1908); 31, 221, 783 (1909); *Ber.*, 40, 3953 (1907).

² *Gazz. chim. ital.*, 37, 32 (1907).

the intramolecular oxidation took place as indicated by the equation



In these experiments the explosions were induced by percussion.

Preparation of Hydrazine Monochlorate.—To prepare 5 g. of hydrazine monochlorate, 6.8 g. of barium chlorate were added to 5.6 g. of hydrazine sulfate; to this were then added 6.4 g. of barium hydroxide, $\text{Ba}(\text{OH})_2\cdot 8\text{H}_2\text{O}$, the precipitated barium sulfate was removed by filtration and the solution was allowed to concentrate by spontaneous evaporation in the open air, at room temperature. All attempts made to crystallize the salt in mass, even at low temperatures over sulfuric acid, resulted in the spontaneous decomposition of the compound with the evolution of chlorine. When evaporated in small bulk on the stage of a microscope, laminated crystals made their appearance, only to decompose at once with the evolution of gas. A slight residue was left which, on examination, proved to be hydrazine chloride.

Experiments 1-4.—A solution of hydrazine monochlorate, prepared as described above, 1 cc. of which contained 0.035 g. of the salt, was treated in accordance with the procedure outlined. The 5 cc. portions, together with 30 cc. of water, were introduced into the distilling flask and the resulting solution was distilled.

On examining the distillate, no indication of the presence of hydronitric acid in any fraction was obtained.

Experiments 5 and 6.—Conditions identical with those of the preceding experiments were chosen except that in each of these cases 0.5 cc. of concentrated sulfuric acid was added. The distillate was caught in each experiment in 5 cc. fractions, in each of which the presence of hydronitric acid was clearly demonstrated. The amounts of acid increased as the distillation progressed until the last fraction was reached, in which no indication of the presence of the acid could be obtained.

Decomposition of a Solution of Hydrazine Dichlorate.—A solution of hydrazine dichlorate was prepared by treating 3.2 g. of hydrazine sulfate with 7.9 g. of barium chlorate. The solution was filtered and was concentrated by evaporation at room temperature until 1 cc., as shown by analysis, contained 0.05 g. of hydrazine dichlorate. Treatment of small portions of the solution with sulfuric acid and with barium chloride, respectively, gave no indications of the presence of appreciable quantities of barium or of sulfuric acid.

In concentrated solution this compound likewise proved so unstable that it rapidly decomposed. Crystals could be obtained when small amounts of the solution were evaporated to dryness under the microscope, but their disintegration was so rapid that they could not be subjected to an examination. Here, also, a slight, solid residue, consisting of a chloride of hydrazine, remained from the destruction of the compound. The main products of the decomposition of hydrazine dichlorate, as is also true of the monochlorate, are gaseous.

Experiment 7.—A 5 cc. portion of the above solution, with 30 cc. of H_2O , was distilled and collected in 5 cc. fractions. Appreciable quantities of hydronitric acid were formed, the most distinct indications of its presence being obtained in the sixth fraction.

Experiment 8.—The conditions prevailing in Expt. 7 were closely duplicated except that 0.5 cc. of concentrated sulfuric acid was added to the solution. Hydronitric acid was found to be present in the successive fractions of the distillate in increasing amount up to the fifth fraction. The last fraction, containing other products of the reaction, gave no indications of the presence of the acid.

Decomposition of a Solution of Hydrazine Monoperchlorate.—This substance was prepared by Salvadori¹ and by the author independently. Salvadori ascribed to it the formula $N_2H_2ClO_4 \cdot \frac{1}{2}H_2O$, a formula upheld by his analytical results. The salt readily can be crystallized from water on the water bath, which fact bespeaks for its remarkable stability. It is nonhygroscopic, soluble in water and alcohol and insoluble in ether, carbon disulfide, benzene and chloroform. It melts at $131-132^\circ$. Like the chlorate, hydrazine monoperchlorate on heating and on being subjected to percussion is violently explosive.

A solution of this compound was obtained by treating 3.3 g. of hydrazine sulfate with 4.3 g. of hydrated barium hydroxide and 4.3 g. of barium chlorate, in solution. After the barium sulfate had been removed by filtration, the solution of hydrazine monoperchlorate was evaporated until the compound crystallized out. As a check upon the purity of the compound so obtained, the percentage of nitrogen was determined by the method of Rimini.²

Per cent. nitrogen: calculated for $N_2H_2ClO_4 \cdot H_2O$: 11.17%; found (av. of two): 10.51%.

Determinations of so-called water of crystallization by desiccation methods shown in Table I, made before the appearance of Salvadori's work, had led us to the belief that the monoperchlorate crystallized with one molecule of water of crystallization.

TABLE I.

| No. | $N_2H_4 \cdot HClO_4 \cdot H_2O$ Weight taken. | Loss. | Theory. | |
|--------|---|--------|----------------------|------------|
| | | | $\frac{1}{2} H_2O$. | 1 H_2O . |
| 1..... | 0.2737 | 0.0175 | 0.0128 | 0.0196 |
| 2..... | 0.5194 | 0.0335 | 0.0193 | 0.0372 |

In Experiment 1 the sample was dehydrated to constant weight over sulfuric acid; in Experiment 2 the sample was heated at 100° on a water bath until its weight became constant. These results show that the water is quite readily removed from the monoperchlorate, both by desiccating agents and by heat. No attempt is here being made to refute the statements of Salvadori.

¹ *Loc. cit.*

² *Gazz. chim. ital.*, 29, I, 265 (1899); *Atti. accad. Lincei*, [5] 15, II, 320; *Zentr.*, 11, 1662 (1906).

Experiments 9 and 10.—A volume of 25 cc. of a solution of hydrazine monoperchlorate containing 0.004 g. per cc. was distilled until the solution came to dryness. Collected in 5 cc. fractions. No test for hydronitric acid was obtained in any fraction. On coming to dryness, the residue exploded. From the products of the decomposition remaining in the flask, after being dissolved in water, were obtained, by means of the usual tests, indications of the presence of hydrochloric acid and hydrazine. The last fraction of the distillate gave an acid reaction and emitted the odor of chlorine.

Experiments 11 and 12.—In these experiments the conditions which obtained in Experiments 9 and 10 were observed as closely as possible, with the single exception that 0.5 cc. of concentrated sulfuric acid was added to the solution before the distillation. No test for hydronitric acid was obtained in any fraction. The last portions of the distillate gave an acid reaction with litmus. Some sulfur dioxide was produced. The residue in the flask consisted of hydrazine sulfate and gave no tests for chlorine ions.

Decomposition of a Solution of Hydrazine Diperchlorate.—To prepare 10 g. of hydrazine diperchlorate, 13.5 g. of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ were neutralized with perchloric acid which had been freed from hydrochloric acid by precipitation with a solution of silver perchlorate, prepared by dissolving silver carbonate in perchloric acid. To the solution of barium perchlorate thus formed was added the theoretical amount, 5.56 g., of hydrazine sulfate. After removing by filtration the precipitated barium sulfate, the clear solution was evaporated to dryness over steam coils and with the aid of a blast of dry air.

Experiments 13-16.—Distillation of the unacidified (Expts. 13 and 14) and the acidified (Expts. 15 and 16) solutions, respectively, gave no detectable amount of hydronitric acid. The residue from the former showed the presence of hydrazine and of chloride; that from the latter, hydrazine sulfate.

Decomposition of Solids.

The apparatus used for the decomposition of the solid substances consisted essentially of three parts, which, in the order in which they were connected, were (1) a carbon dioxide generator, especially constructed with a view to furnishing very pure, air-free gas, (2) an ignition tube, containing a thermometer, in which the substance under examination was heated, and (3) an absorption apparatus, designed for the subsequent detection of hydronitric acid.

The absorption apparatus, connected with the farther end of the ignition tube, consisted of two large test tubes, each of which contained a few cubic centimeters of distilled water. These were so connected by means of glass tubes and stopcocks that the current of gas could be passed either through the two tubes in series, or through the farther tube only. By this device it was possible to prevent the contamination of the solution to be tested for hydronitric acid by other products formed at certain stages of the decomposition. After the current of gas had passed through the two tubes it entered the third, to the inside wall of which were fastened several strips of filter paper impregnated with manganous sulfate.

By moistening one of these slips with a few drops of potassium hydroxide solution, introduced through a small separatory funnel, it was possible to detect the presence of oxygen in the tube at any time. To facilitate the successive application of this test without dismantling the apparatus, the stem of the separatory funnel was bent at right angles. By slightly turning the funnel, the end of the stem could be brought into contact with successive strips of the paper.

The gas finally passed through a short tube into a eudiometer filled with a solution of potassium hydroxide.

Procedure Followed.—When the air in the entire apparatus had been displaced by carbon dioxide, as indicated by the failure to obtain a brown coloration on the manganous sulfate paper, heat was applied slowly to a weighed sample of the hydrazine salt contained in a porcelain boat, which previously had been introduced into the ignition tube. A slow stream of carbon dioxide was passed through the apparatus throughout the decomposition of the salt and until all decomposition products had been swept into the absorption apparatus. When it became evident in any case that products of decomposition capable of interfering with the detection of hydronitric acid were being formed in any considerable quantity, the current of gas which previously had passed through both absorption tubes was directed so as to pass through the second only. By this means the hydronitric acid, which seemed ordinarily to be formed in the early stages of the decomposition, was not contaminated by the products of the final stages.

The acid was identified by the usual method. The unabsorbable, gaseous products of decomposition were collected in the eudiometer and, whenever it seemed desirable, were subjected to further examination.

Decomposition of Hydrazine Monoperchlorate. Experiment 17 (and duplicate, 18).—A sample of hydrazine monoperchlorate of 0.10 g. was treated as outlined under "procedure." The salt first melted, then began to boil slowly, giving off gas and water vapor. At this stage of the decomposition, as shown by the reddening of the ferric chloride in the first of the absorption tubes, hydronitric acid was produced.

When the visible evolution of gas from the substance undergoing decomposition had ceased, as marked by the cessation of the formation of bubbles, the course of the stream of gas through the apparatus was diverted into the second absorption tube. On further heating then, the substance in the boat exploded, emitting light, and filling the apparatus with fumes (H_2O and HCl ?) which soon condensed. It was subsequent to this violent stage of the decomposition that a nonabsorbable gas appeared in the eudiometer. A slight, white residue was left.

The solution from the second absorption tube, on examination, showed the presence of chlorine ions with silver nitrate in the presence of nitric acid; of hydrogen ions, with blue litmus; of chlorine, with potassium iodide and carbon disulfide and, perhaps, of nitrates. Water was a further product of the decomposition. The gas accumulated in the eudiometer at the end of the run proved to be 14.0 cc. of nitrogen, and 7.6 cc. of oxygen. The presence of oxygen was indicated also by the manganous sulfate paper.

Decomposition of Hydrazine Diperchlorate. Experiment 19 (and duplicate, 20).—Following the procedure already described for preceding experiments, a portion of hydrazine diperchlorate of 0.057 g. was decomposed and its decomposition products studied. These proved to be hydronitric acid in considerable quantities; oxygen, chlorine, and chlorine and hydrogen ions, as determined by the usual tests. The unabsorbed gases proved to be 9.0 cc. of nitrogen, and 8.0 cc. of oxygen.

This substance in decomposing behaved very much as did the monopерchlorate in that the decomposition at first was gradual and was accompanied by a slow bubbling. After this had ceased an explosion occurred which filled the tube with a yellow-green gas of chlorine or of chlorine peroxide, or both. The odor indicated chlorine peroxide. It was subsequent to the explosion, also in this case, as in the preceding instance, that the nitrogen and oxygen made their appearance in the gas collector, a fact which would indicate that they were liberated at the time of the explosion. A white residue, presumably of ammonium chloride, remained.

Action of Potassium Perchlorate upon Hydrazine Sulfate. A Correction.—In connection with their study of the oxidation of hydrazine,¹ Browne and Shetterly found that potassium perchlorate (Baker and Adamson, "C. P."), when used in comparatively large quantities, oxidized hydrazine in sulfuric acid solution, with formation of both hydronitric acid and ammonia. The former product, under most favorable conditions, was obtained in exactly the same amount, 22.4%, with potassium perchlorate, as with potassium chlorate² as oxidizing agent. The possible significance of this fact was overlooked until the attention of one of the authors was directed to the matter by Dr. H. H. Willard, who has done extensive work with the perchlorates.³ Dr. Willard very kindly furnished a liberal sample of the very pure potassium perchlorate prepared during the course of his investigations.

In a series of additional experiments performed by Dr. Shetterly under conditions similar to those prevailing in the earlier work, except that the very pure potassium perchlorate, which was found to be entirely free from chlorates, was used, no indication whatever of the oxidation of the hydrazine was obtained. The tests for both hydronitric acid and ammonia gave negative results. Examination of two samples of the Baker and Adamson perchlorate used in the earlier work showed that this product contained a considerable quantity of potassium chlorate (KClO_3 found, (1) 4.22, (2) 4.23%). It may, therefore, be concluded that chlorate-free potassium perchlorate is without action upon hydrazine sulfate under the conditions of the experiments, and that the oxidizing action noted in the earlier experiments was due to the presence of potassium chlorate in the perchlorate used.

This conclusion is of particular interest when considered in connection with the results obtained in the decomposition of the perchlorates of

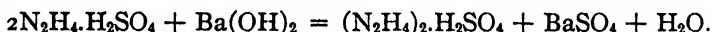
¹ THIS JOURNAL, 31, 221-37 (1909), page 233.

² *Ibid.*, 30, 53-63 (1908), page 57.

³ Richards and Willard, *Ibid.*, 32, 4 (1910); Willard, *Ibid.*, 34, 1480 (1912).

hydrazine. The formation of hydronitric acid in this decomposition in the dry way suggests the query: Is this formation not due to the action of the chloric acid radical on the hydrazine instead of the perchloric radical? It may be regarded as possible that the decomposition of the perchlorate takes place in such a way that its initial stage is marked by the liberation of oxygen, yielding chlorate, a decomposition characteristic of the more stable perchlorates, and that the chlorate in turn reacts intramolecularly to form hydronitric acid. The presence of free oxygen in the gaseous products of the decomposition may be interpreted to indicate such a liberation. The freedom from chlorate of the hydrazine perchlorates dealt with is suggested by the absence of hydronitric acid from the products obtained from these when decomposed in the wet way, a suggestion borne out by their analysis.

Decomposition of Hydrazine Monosulfate.—Hydrazine monosulfate was prepared by treating 2.28 g. of hydrazine disulfate in solution with a solution of barium hydroxide containing 2.76 g. of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ transposition taking place analytically according to the equation



After filtering, the clear solution was evaporated over steam coils. A clear syrup, or gum, resulted which, on being touched with spatula or rod, rapidly became an opaque mass of white crystals, the crystals growing out in fronds from the point of the surface to which the rod had been touched. The analysis of the dry substance gave the following:

N calc. for $(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$: 34.52; found (av. of 4): 33.45%. S calc.: 19.76; found (av. of 2): 19.76%.

Experiment 21.—A portion, 0.2 g. in weight, when heated gradually, melted at $70-80^\circ$ and at 120° began to decompose, as evidenced by the appearance of a white sublimate on the cooler portions of the combustion tube. It was not until a temperature of 160° was reached, however, that the decomposition became so rapid as to produce frothing. The sublimate then became yellow, revealing its identity as sulfur. When the temperature had been raised to 180° the visible activity had ceased. There was a free evolution of water and hydrogen sulfide. No test for hydronitric acid, on account of the presence of hydrogen sulfide, could be obtained. A white residue remained which, qualitatively, proved to be hydrazine sulfate.

Experiment 22.—Experiment 21 was duplicated with modifications designed to test successive portions of the gaseous products of the decomposition, still yielding negative results with respect to hydronitric acid.

It was noticed that as the condensed moisture on the inside of the tube was driven out by re-evaporation, a white crystalline substance remained. On examination, this substance was shown to be ammonium carbonate.

Decomposition of Hydrazine Disulfate. Experiments 23 and 24.—Hydrazine disulfate in 1 g. portions, finely pulverized, was subjected to decomposition under the conditions shown above. Once the temperature of incipient decomposition had been reached, the intramolecular oxidation became self-propagating. There ensued a lively evolution of gas accompanied by a bubbling of the melted mass. Sulfur was evolved and formed an abundant white sublimate, deepening to a yellow color where the sub-

limate was thickest, over the interior of the apparatus. Water was formed. And among the gaseous products of the decomposition were found volumes of hydrogen sulfide and sulfur dioxide.

No hydronitric acid was found in any experiment with the disulfate.

Sulfurous acid gives a reaction with both silver nitrate and ferric chloride which superficially resembles and effectively masks that of the hydronitric acid with these reagents—namely, a white precipitate with silver nitrate, which gives a red coloration when treated with ferric chloride, and a red coloration direct with ferric chloride, due to the formation of ferric sulfite. Practically the only differences which easily are shown between the reactions of sulfur dioxide and hydronitric acid with these two favorite reagents for the detection of hydronitric acid are that silver trinitride is readily and violently explosive, while silver sulfite is not and that the color obtained from ferric chloride and hydronitric acid, due to ferric trinitride, slowly fades, while that due to ferric sulfite fades more rapidly. The change of color in solution of ferric sulfite is brought about by the reduction of the ferric iron to the ferrous by the sulfite and the oxidation of the sulfite to the sulfate by the ferric iron. Ferrous sulfate results.

It is necessary, therefore, if one is to test for hydronitric acid in the presence of sulfur dioxide, first to eliminate the sulfur dioxide. The method as applied in the following paragraphs is recommended.

A Test for Hydronitric Acid in the Presence of Sulfitcs.

To 10 cc. of a standard solution of hydronitric acid were added 100 cc. of a 5% solution of sodium hydroxide, 10 cc., 10% sodium sulfite solution and 15 cc. of a 3% solution of hydrogen peroxide. This solution was boiled until effervescence had ceased upon which it gave negative tests for both hydrogen peroxide and sulfites with the potassium iodide and potassium iodate tests, respectively. The solution was then transferred to a distilling apparatus and, after acidification, it was distilled until a few drops of the distillate gave no test for hydronitric acid. To the distillate were then added 10 drops of ferric chloride and the solution was diluted with distilled water to a definite volume. Another portion of 10 cc. of the standard solution of hydronitric acid was then treated with the same amount of ferric chloride and was diluted to an equal volume. The two solutions were then compared in comparison cylinders and their color intensity was found to be equal, showing that no hydronitric acid was oxidized by hydrogen peroxide in alkaline solution.

The solution from the absorption apparatus, which contained the decomposition products of the hydrazine disulfate, was then treated with 10 cc. of a 5% solution of sodium hydroxide, and 10 cc. of a 3% solution of hydrogen peroxide. The resulting solution was placed in a distilling apparatus and boiled until effervescence had ceased. The cessation of the effervescence in this case was taken as an indication of the complete

removal of the excess of hydrogen peroxide. The solution was then acidified with 1 : 1 sulfuric acid and was distilled. The distillate gave no tests for hydronitric acid with ferric chloride.

Summary.

The decomposition of hydrazine monochlorate, by heat, in neutral, aqueous solution yielded no hydronitric acid; in (H_2SO_4) acid solution hydronitric acid resulted. The corresponding di-salt yielded hydronitric acid both in the presence and absence of sulfuric acid. The mono- and diperchlorate of hydrazine yielded no hydronitric acid in either acidified or unacidified solution. When the dry crystallized salt was decomposed by heat in a stream of carbon dioxide, hydronitric acid was produced from the latter, but not from the former. Both liberated gaseous chlorine, nitrogen and oxygen, and chloride and hydroxide ions. The mono- and disulfates of hydrazine, under similar conditions, gave off water, hydrogen sulfide, sulfur dioxide and sulfur, but no hydronitric acid. A method is described for the detection of hydronitric acid in the presence of sulfur dioxide.

CORNELL UNIVERSITY, ITHACA, N. Y.

ELECTROCHEMICAL OXIDATION OF HYDRAZINE SULFATE AND AMMONIUM HYDROXIDE.¹

By J. W. TURRENTINE AND J. M. OLIN.

Received December 15, 1914.

Szarvasy² has shown that hydrazine, on electrolysis, yields nitrogen at the anode and hydrogen at the cathode in the ratio in which these two elements exist in the hydrazine molecule, namely, $\text{N}_2 : 2\text{H}_2$. These results were obtained from the electrolysis of solutions of hydrazine hydrate, sulfate and chloride at varying concentrations of solution, current densities and temperatures. The hydrazine cations, he explains, are oxidized at the anode by the discharge anions, oxygen, chlorine, with the formation, respectively, of water and hydrochloric acid, evolving nitrogen; and at the cathode "the free base reacts with two molecules of water, the hydrate being re-formed and hydrogen liberated." Under the conditions of his experiments, as his figures indicate, the hydrazine cation was oxidized at the anode quantitatively to nitrogen without any indication of a reduction at the cathode.

These experiments show conclusively that oxygen and chlorine liberated by electrolysis, under the conditions named, do not oxidize hydrazine in the alkaline solution of the hydrate or in the neutral or weakly acid solution

¹ In part a chapter from the thesis submitted by the author to the Faculty of Cornell University for the degree of Doctor of Philosophy, May, 1908.

² "Electrolysis of the Nitrogen Hydrides and of Hydroxylamine, *J. Chem. Soc.*, [1] 11, 603 (1900).

of the sulfate or chloride¹ to an intermediate oxidation product as ammonia or hydronitric acid, but, as stated above, directly to nitrogen.

The investigation here described was undertaken by the present writer to discover if, under more widely varying conditions than those which obtained on the work of the investigation quoted, reactions could not be induced by electrolysis, as the primary agent, which would yield as a product other hydronitrogens such as ammonia, and more particularly, hydronitric acid.

Looking upon the action of the current at the anode as nothing more than that of an agent whose function it is to liberate in that area some oxidizing agent such as oxygen, chlorine, etc., and wishing to simulate as closely as possible a weak oxidizing agent, as one would conclude from the complete oxidation of the hydrazine directly to nitrogen in the experiments of Szarvasy that the conditions there were such as to yield too strong an oxidizing agent, the electrolysis was conducted, in our earlier experiments, between a large anode and small cathode and with a very low current density at the anode. The small cathode was employed to cut down the reduction in its region.

The electrolysis of the hydrazine sulfate was conducted in strongly acid solutions, since, as observed by Browne and Shetterly² in their work on the oxidation of hydrazine, the production of hydronitric acid and ammonia is always most noticeable in strongly acid solution. Moreover, to remove readily the hydronitric acid from its aqueous solution, it is quite advantageous to acidify strongly before distillation. It was hoped thus by acidification and heating to drive off the acid, if formed, from the electrolytic bath as rapidly as produced, as it has been shown³ that hydronitric acid itself is decomposed electrolytically at the anode.

Experimental.

Experiment 1.—A solution of hydrazine disulfate, saturated in the cold, containing 5% by volume of concentrated sulfuric acid, was electrolyzed at its boiling point between platinum electrodes and contained in the apparatus described as follows:

A 250 cc. beaker contained as anode a sheet of platinum foil of 60 cm. square, on a face, curved so as to fit against the walls of the beaker, and a platinum wire cathode extending horizontally to the center of the beaker and then perpendicularly down. The beaker rested on a sand bath and was covered as tightly as possible by an evaporating funnel. From the top of the funnel extended a Reitmeyer bulb to return any acid spray. From this a narrow glass tube extended downward to the bottom of a test

¹ The author makes no mention in connection with the chloride and sulfate of hydrazine as to whether he dealt with the neutral, monosalt or the acid disalt.

² "On the Oxidation of Hydrazine, I," *THIS JOURNAL*, 29, 1305 (1907); II, *Ibid.*, 30, 53 (1908); III, *Ibid.*, 31, 221, 783 (1909).

³ Szarvasy, *Loc. cit.*; Peratoner and Oddo, *Gazz. chim. ital.*, 25, II, 13; 30, II, 95.

tube containing a few cubic centimeters of an aqueous solution of ferric chloride. The test tube was closed by means of a two-hole rubber stopper and was connected in turn through a suction flask, to a Bunsen pump. This complication in the apparatus was introduced to make it possible, by drawing a rapid stream of air into the funnel from the edges of the beaker and on through the test solution of ferric chloride, to catch and detect any hydronitric acid distilled from the solution during the electrolysis. The liquid from the condensed vapors was conducted from the collecting rim of the funnel likewise to a test tube containing a test solution of ferric chloride.

The solution of above composition was poured into the electrolytic cell until it covered the entire anode and submerged 1.5 cm. of the wire cathode; its temperature was then raised to its boiling point and there maintained throughout the electrolysis. Distilled water was added from time to time to prevent too great concentration. The current density at first was regulated so that only the slightest evolution of gas was visible at the anode. Under these conditions no indication of the presence of hydronitric acid could be found in either test solution.

The current density was subsequently raised, but with only negative results.

Experiments 2, 3 and 4.—The concentration of the sulfuric acid in the solution undergoing electrolysis was increased successively to 10%, 15% and 20%, respectively, in these experiments, but only negative results as regards the formation of hydronitric acid were obtained. No tests were made for ammonia.

These negative results made it appear improbable that the direct oxidation of the hydrazine cation by the oxygen set free by the current could be made to yield readily the less highly oxidized products of hydrazine as hydronitric acid and ammonia. Oxygen, in its active condition as evolved from the anode, apparently is too strong an oxidizing agent, carrying the oxidation to the extreme of removing all the hydrogen atoms from the union with nitrogen atoms in the hydrazine molecule. The conditions of the experiments were then so altered as to permit of the formation in the electrolytic bath of oxidation products which would escape from the sphere of action less readily than the oxygen. The oxidation products could then, by secondary reactions, subsequently, or during the electrolysis, oxidize the hydrazine.

The oxidation products formed from the electrolysis of solutions in which $\text{SO}_4^{=}$ ions predominate are ozone (H_2O_3) and persulfuric acid. These are produced in largest amounts at high current densities. Accordingly, a long, thin, platinum wire anode, encircling the cup and exposing an active surface for about 10 cm. of its length, was substituted for the large sheet anode in the electrolytic cell, as described in Experiment 1.

In every other respect the cell was allowed to remain as originally described.

Experiment 5.—A saturated solution of hydrazine sulfate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, containing 10% by volume of concentrated sulfuric acid, was electrolyzed with a current of 1.5 amperes. As the electrolysis continued, the solution became heated. Ozone was evolved.

Hydronitric acid soon made its appearance both in the gases and distillate from the cell and continued to come over during the electrolysis. Strong tests were obtained with solutions of ferric chloride and silver nitrate.

Experiment 6.—This experiment was a duplicate of Experiment 5, with the modification that the temperature of the solution in the cell was maintained at the boiling point from the beginning of the electrolysis. Both the gases and distillate products contained hydronitric acid, though only in small amounts.

It was feared that under the conditions of this experiment the hydronitric acid might be oxidized in its vaporous form by the ozone evolved with it,¹ thus accounting for the low yield of the acid. It seemed desirable, therefore, to conduct the electrolysis at so low a temperature that the acid would remain in solution. The experiment was designed, also, with a view to determining whether hydronitric acid was produced at low temperatures and, as indicated by Experiment 5, continuously during the electrolysis.

Experiment 7.—A solution of the same composition as that used in the previous experiments was electrolyzed in the cell as described, its temperature being maintained during the electrolysis, by means of an ice bath, at 0° and below. The presence of the acid in the gases drawn from the cell could not be detected. There was a free evolution of ozone.

The electrolysis was then discontinued, and to test the cold solution for the presence of hydronitric acid the solution was transferred to a 500 cc. distilling flask. Through the mouth of the flask to the bottom extended a glass tube. The side arm of the flask was connected to a condenser, the lower end of which was joined, by means of an adapter, to a suction flask which in turn was connected with a Chapman pump. In the suction flask was held a small test tube containing the test solution of ferric chloride into which dipped the elongated tube of the adapter. Air was then drawn through the cold solution and was caused to bubble through the ferric chloride solution in the test tube, thus sweeping the hydronitric acid from the acid solution through the test solution.

While a distinct test was obtained, only a small amount of hydronitric acid was thus detected. The solution was then heated to boiling, the dis-

¹ It may be questioned and remain undetermined whether the ozone could escape from the solution at the temperature at which the electrolysis was conducted without undergoing instantaneous decomposition.

distillate was caught in 5 cc. fractions and each tested with 6 drops of ferric chloride. A series of strong tests for hydronitric acid was thus procured.

The foregoing experiments tended to show that hydronitric acid was produced in the electrolytic bath during the electrolysis either directly, *i. e.*, by the direct oxidation of the hydrazine cation by oxygen, which seemed impossible in the light of previous experiments, or by secondary reactions with other anode products.

So far only qualitative determination had been made of the yield of acid. To obtain quantitative measurement Experiment 8 was performed.

Experiment 8.—In the apparatus and under the same conditions of temperature as described under Experiment 7 a solution of the disulfate containing exactly 1.00 g. of the salt in 150 cc. H_2O and 50 cc. concentrated H_2SO_4 was electrolyzed for six hours with a current which varied from 0.5 to 1.5 amperes.

For the ferric chloride solution, formerly placed in the test tube to catch and detect vapors of hydronitric acid in the gaseous products of the electrolysis, was substituted a few cubic centimeters of a solution of silver nitrate containing sodium acetate, prepared by adding to 2 cc. of a 10% solution of AgNO_3 , 2 cc. of a 10% solution of sodium acetate, and sufficient water to completely dissolve the silver acetate formed. During the course of the experiment a slight precipitate of silver trinitride appeared in this tube. At the end of the electrolysis the solution was transferred to the distilling apparatus mentioned under Experiment 7. The tube of the adapter dipped beneath the surface of a solution of AgNO_3 , prepared as above, so that both liquid and vapor products of the distillation could be recovered. A copious, white precipitate of AgN_3 was formed in the receiver. When the distillate no longer showed the presence of hydronitric acid, when subjected in small amounts to the ferric chloride test, the solution was again made up to 200 cc. with distilled water, and two 2 cc. portions, each equal to 0.01% of the total sample, were withdrawn for analysis. The average of the two analyses gave 0.00729 g. of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$ in 2 cc., making the value of the total solution 0.729 g. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$. This value, subtracted from the total amount (1.00 g.) started with, gave the weight of the salt oxidized as 0.271 g. of $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$. The silver trinitride was filtered on a Gooch filter, quickly washed with small amounts of distilled water, dried at 110° and weighed. Weight of $\text{AgN}_3 = 0.0464 \text{ g.} = 0.0130 \text{ g. HN}_3$.

Experiments 9 and 10.—The solution that remained from Experiment 8 was subjected to two successive treatments as described under Experiment 8, the electrolysis in each case being prolonged for a period of three hours, with a current of 1.0 to 1.5 amperes. After each distillation the solution was made up again carefully to its original volume and samples were withdrawn for analysis. The silver trinitride also was determined

in both cases as above. The results of these two experiments, with those of two others, are given in Table I.

TABLE I.
Amount $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$.

| No. | Before electrolysis. | After electrolysis. | Oxidized. | Weight AgN_3 . | Weight HN_3 . | Per cent. HN_3 . |
|---------|----------------------|---------------------|-----------|-------------------------|------------------------|---------------------------|
| 8..... | 1.00 | 0.729 | 0.271 | 0.0464 | 0.013 | 29.0 |
| 9..... | 0.714 | 0.432 | 0.282 | 0.0470 | 0.0132 | 28.3 |
| 10..... | 0.423 | 0.000 | 0.423 | 0.0576 | 0.0161 | 23.0 |
| 11..... | 0.50 | 0.000 | 0.50 | 0.0838 | 0.0235 | 28.4 |

For the sake of comparing these results with those obtained in the purely chemical oxidation, the yields of hydronitric acid have been calculated on the basis of the equation:



During the oxidation of hydrazine by purely chemical means ammonia seems invariably to be formed under the conditions favorable to the production of hydronitric acid. In order to ascertain whether this same general principle is applicable to the electrolytic oxidation of hydrazine, a portion of the residual solution from which all the hydrazine and hydronitric acid had previously been eliminated, as described above, was made alkaline with potassium hydroxide and distilled in the usual way, the ammonia being caught in a measured excess of standard hydrochloric acid. By titrating back with standard alkali, it was found that about 0.05 g. of NH_3 had been formed during the decomposition of about 1.5 g. $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, corresponding to a yield of about 51% of NH_3 on the basis of the above equation.

The electrolysis of the hydrazine salt in the latter experiments was conducted under conditions chosen with a view to the production of more permanent oxidizing agents than the oxygen evolved from the anode. The fulfilment of our prediction and the success of our efforts indicate from the start that the oxidizing agent which one knows to be formed as anode products under these conditions are the agents which yield HN_3 and NH_3 . Only three oxidizing agents are possible, namely, the oxygen evolved from the anode, the ozone evolved from the anode and dissolving in the solution, and the persulfuric acid also dissolved in solution, both of the latter two being inevitable products of electrolysis under the conditions maintained. The early experiments in this work as well as those of Szarvasy are sufficient to lead one to dismiss oxygen, though no direct proof has been adduced to show that under the conditions of very high current density the hydrazine cation might not be oxidized to other hydro-nitrogens.

Chattaway¹ observes that phenylhydrazine in a liquid film on filter

¹ "Oxidation of Hydrazines by Oxygen," *J. Chem. Soc.*, 91, 1323 (1907).

paper, when exposed to the action of oxygen confined in stoppered bottles, rapidly absorbs oxygen with the production of heat and evolves a volume of nitrogen greater than that of the oxygen absorbed.

The chemical action of ozone on hydrazine has not been studied as yet, but the slight tests for HN_3 obtained from the cold solutions through which ozone, as well as oxygen, had been passing would indicate that neither of these two acted as the oxidizing agent to any great extent.

Browne and Shetterly¹ have shown that persulfates in hot, acid solutions oxidize hydrazine salts, yielding N_2 , HN_3 and NH_3 . The present writer, in his attempts to prepare hydrazine persulfates, has found that persulfates do not oxidize hydrazine readily in the cold. It was only necessary, therefore, to analyze the cold solution before and after the distillation to show whether the major portion of the oxidation had occurred during the electrolysis or during the distillation. That some oxidation occurred during the electrolysis in both hot and cold solution has already been shown. The following experiment was designed to reveal to what extent oxidation occurred during the distillation.

Experiment 11.—A solution which contained 0.50 g. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$, to 50 cc. of concentrated H_2SO_4 and 150 cc. H_2O , was electrolyzed under the same conditions of time, current, etc., as those which obtained in Experiments 9 and 10. After the electrolysis aliquot portions were analyzed for hydrazine; the results of the analysis showed that 0.1976 g. had been decomposed during the electrolysis, leaving in the solution 0.3024 g. unoxidized. The solution was then distilled until all HN_3 had been removed, was diluted again to a known volume and aliquot portions again analyzed. The results showed that all the remaining hydrazine had been consumed during the distillation.

These facts point conclusively to the persulfuric acid as the oxidizing agent, and explain why a stronger test for HN_3 can be obtained from a warm solution during the electrolysis than from the refrigerated one.

These conclusions fail to take into consideration the possible action of ozone and persulfuric acid on HN_3 . Until such a time when we shall understand the chemistry involved in a possible interaction of these substances, we can not say that HN_3 is not a product of the electrolytic oxidation of hydrazine in much greater amounts than indicated in our experiments, and that it is not destroyed almost as fast as formed by ozone or even by the persulfates.

It has been shown² in this laboratory that the oxygen evolved by the decomposition of persulfuric acid, theoretically and experimentally is both analogous and similar to that evolved against an insoluble anode in the electrolysis of a sulfate. Why the oxygen from the anode oxidizes hy-

¹ *Loc. cit.*

² Turrentine, *J. Phys. Chem.*, **11**, 623 (1907).

drazine to N_2 and that from the decomposition of persulfates oxidizes it only to hydronitrogens may be explained on the basis of the principles of mass action. The oxygen evolved against an anode is necessarily in contact with only the merest film of solution containing the oxidizable cations. The migration of the cations away from the anode would tend further to decrease their concentrations in this film. The conditions resulting are those of relatively high concentration of the oxidizing agent and low concentration of the substance oxidized, conditions suitable for complete oxidation. On the other hand, with persulfates in solution in low concentration and more slowly evolving oxygen and hydrazine in high concentration and with its concentration uninfluenced by migratory tendencies incited by the current, the conditions are the reverse of those existing at the anode—the oxidizing agent is present in low concentration and the reducing agent in relatively high concentration, thus affording conditions suitable for mild or incomplete oxidation.

The Electrochemical Oxidation of Ammonia to Hydrazine.¹

Raschig² obtained hydrazine as a product of the chemical oxidation of ammonia when he treated ammonium hydroxide, in 20% solution, with sodium hypochlorite, in normal solution, in the presence of glue. The proportions taken in a typical experiment were, 200 cc. of ammonium hydroxide, 100 cc. (normal) sodium hypochlorite, with 5 cc. of 1% glue solution.

Attempts were made to induce analogous reactions electrochemically by electrolyzing under various conditions solutions of ammonium hydroxide with ammonium or sodium chloride, and glue. The proportions taken were 200 cc. 25% ammonium hydroxide, 100 cc. normal ammonium chloride or sodium chloride, with 5 cc. 2% glue, a solution not widely differing from that employed by Raschig. The strength of the electrolyzing current was varied between 4.5 amperes and 0.3 ampere, the temperature between that of ice and of the boiling point of the solution, and the concentrations of the ammonium hydroxide and glue from zero to that indicated by the above statement of concentrations. These conditions, with either ammonium or sodium chloride, yielded no hydrazine detectable by Fehling's solution. Finally, with sodium chloride, when that solution was added slowly during the electrolysis, the formation of hydrazine took place. The conditions obtaining were as follows: Current strength, 0.3–0.4 ampere; temperature, 100°; strength of solution, that cited above. The sodium chloride solution was added gradually until it totaled 310 cc. To replace the ammonia lost through volatilization, additional volumes of the solution, likewise, were poured in from time to time, until its volume

¹ Experimentation by J. M. Olin.

² *Ber.*, 40, 4580–8 (1907); D. R. P. 198,307.

also totaled 310 cc. The experiments were repeated and the above observations duplicated.

Summary.

Hydrazine, in saturated solution of the sulfate, containing 10% by volume of concentrated sulfuric acid, is oxidized electrochemically to hydronitric acid when a high current density is maintained at the anode. The yield in hydronitric acid is greater when the solution undergoing electrolysis is held at a low temperature (0°). Since these are the conditions favoring the formation of persulfates, it is believed that the oxidation is the product of a secondary anode reaction, the action of the persulfate ion, a product of a primary anode reaction, on the hydrazine ion. The degree of oxidation has been determined.

Ammonium hydroxide, in the presence of sodium chloride and glue and with low current density, is oxidized electrochemically to hydrazine, provided the solution of sodium chloride is added in small amounts at intervals during the electrolysis.

CORNELL UNIVERSITY, ITHACA, N. Y.

A DESCRIPTION OF THE NEW COMPOUND, HYDRAZINE DIPERCHLORATE.¹

By J. W. TURRENTINE (with crystallographic notes by A. C. GILL).

Received November 14, 1914.

While perchloric acid is perhaps the most stable of the oxyacids of chlorine, yet it is a sufficiently strong oxidizing agent, especially in concentrated solution, to lend especial interest to a compound which it can form by union with so unstable and easily oxidizable a base as hydrazine. In even greater degree is this true of the salt formed from chloric acid and the base, hydrazine.

Actuated by such considerations, a research was undertaken in this laboratory, which was originally intended to embrace an investigation of the methods of preparation and the properties of the series of hydrazine salts, the mono-, and dichlorates, and the mono-, and diperchlorates. The work had progressed to a satisfactory stage, all four substances having been prepared and studied in varying degree and the two more stable ones, the perchlorates, having been purified and analyzed, when Salvadori² announced his complete research in an article replete with data on the more stable of both of the chlorates and perchlorates, the mono-salts. No further work has been done in this laboratory, therefore, on either of the compounds studied by him, though our probably more casual observations in some minor details do not coincide with those of the author referred to.

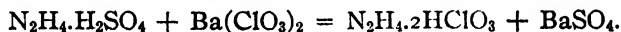
¹ A chapter from the thesis of the author submitted to the Faculty of Cornell University, May 1908, for the degree of Doctor of Philosophy.

² *Gazz. chim. ital.*, 37, 32 (1907).

Salvadori prepared hydrazine monochlorate by treating a solution of chloric acid of known concentration with such a volume of a solution of hydrazine hydroxide as contained an amount of the base equivalent, molecule per molecule, to the chloric acid. After evaporation to an oily consistency over sulfuric acid, the salt was precipitated from the solution by the addition of alcohol and was washed with absolute alcohol. Laminated crystals were obtained. These were shown to be soluble in water, less soluble in alcohol and insoluble in ether, benzene, and chloroform. The salt proved to be instable and easily explosive on being subjected to a percussion.

The monoperchlorate of hydrazine was obtained in crystalline form directly from evaporation on the water bath. It crystallizes from water with one-half molecule of water of crystallization. It melts at $131-2^{\circ}$; at 13° water dissolves 67.56% by weight of the salt. The compound was further studied with a view to its explosibility, its rate of decomposition being determined. The explosion of this compound, when induced by percussion, is said to be equal to that of the perchlorate in violence.

Hydrazine Dichlorate.—This compound was prepared by treating a solution of hydrazine disulfate with the theoretical amount of barium chlorate in solution, the reaction taking place in agreement with the equation,



The barium sulfate was removed by filtration. The filtrate was subjected to qualitative tests for both sulfate and barium and was found to be free from these two most probable impurities. Portions of this solution were then evaporated *in vacuo* over concentrated sulfuric acid, the temperature of the solution being maintained most of the time at 0° , or below. On the appearance of crystals in the concentrated solution, decomposition began to occur with the evolution of chlorine gas and continued with accumulating rapidity, finally resulting in the entire destruction of the hydrazine compound present. When the crystallization was allowed to take place under the microscope, a similar decomposition took place so that the compound could not be further studied there. Attempts to study the crystallized compound were not made.

Hydrazine Diperchlorate.—Hydrochloric-acid-free perchloric acid was obtained on treating a solution of perchloric acid contaminated with hydrochloric acid, a decomposition product, with a solution of silver perchlorate. The latter was prepared by dissolving silver carbonate in perchloric acid; it was added titrimetrically to the impure acid until the last drop produced no further precipitation of silver chloride. By means of the purified acid a solution containing 13.5 g. of barium hydroxide, $\text{Ba}(\text{OH})_2\cdot\text{H}_2\text{O}$, was neutralized and was then treated with the theoretical amount of hydrazine sulfate, 5.56 g. $\text{N}_2\text{H}_4\cdot\text{H}_2\text{SO}_4$, in solution to form

hydrazine diperchlorate. After filtering to remove barium sulfate and after testing the solution for traces of sulfate and barium, the solution was evaporated to crystallization.

In the earlier part of this work the solutions of the diperchlorate were evaporated in desiccators over concentrated sulfuric acid and under reduced pressure. But when it was found that the substance was so stable as to permit it, the evaporations were conducted more expeditiously on the water bath, or on steam coils with the aid of an air blast. When evaporated in this way until crystallization begins to take place and then cooled the entire mass becomes solid with laminated crystals. If evaporated more slowly, beautiful, brilliant plates may be obtained.

Hydrazine diperchlorate crystallizes with two molecules of water of crystallization. This was determined by desiccating *in vacuo* over sulfuric acid, until there was no further change in weight, a carefully weighed sample of the crystals which previously had been allowed to come to constant weight in the open air of a dry, steam heated room. Table I gives the figures obtained.

TABLE I.

| No. | Wight sample. Gram. | Loss. Gram. | Percentage loss. | Theory for 2 H ₂ O. |
|--------|------------------------|----------------|---------------------|-----------------------------------|
| 1..... | 0.1065 | 0.0136 | 12.77 | 13.35 |
| 2..... | 0.1499 | 0.0190 | 12.65 | 13.35 |

Upon dehydration the crystals effloresced. The effloresced salt, however, did not regain its water of crystallization when again exposed to the open air of the laboratory. It is probable, therefore, that the low results were due to a partial dehydration of the crystals before they were transferred to the desiccators.

Analysis.—The nitrogen content of the diperchlorate was determined by the method described by Rimini.¹ The samples for analysis were dissolved in about 25 cc. of water in tall, narrow mouthed Erlenmeyer flasks. An excess of a standard solution of potassium iodate was then run in from a buret. After boiling off the liberated iodine, the solution was cooled and was mixed with 15 cc. 1 : 4 sulfuric acid. Sufficient potassium iodide in crystalline form was then added to completely decompose the excess of iodate and also to dissolve readily the liberated iodine; thereupon the free iodine was rapidly titrated, with starch solution as indicator, with a standard solution of sodium thiosulfate.

TABLE II.

| | | | | | | | | |
|----------------------|--------|--------|-------------|--------|--------|--------|--------|--------|
| Weight taken, g..... | 0.0201 | 0.0201 | 0.0201 | 0.0201 | 0.0201 | 0.0201 | 0.0117 | 0.0117 |
| Nitrogen found..... | 11.00 | 10.23 | 11.00 | 10.85 | 10.48 | 10.41 | 10.41 | 10.14% |
| Average..... | 10.56% | | Theory..... | | 10.41% | | | |

¹ *Gazz. chim. ital.*, [1] 29, 265 (1899); *Atti. accad. Lincei*, [5] 15, II, 320; *Chem. Zentr.*, 11, 1682 (1906).

Chlorine was determined in the perchlorate by the following method: A weighed sample of the salt was transferred to a platinum crucible and was intimately mixed with ten times its weight of pure, chlorine-free sodium carbonate. On account of the difficulty of mixing the dry crystals of the salt with the sodium carbonate and the danger of an explosion on grinding the salt in a mortar, the crystals, after being transferred to the crucible, were dissolved in a drop of warm water and the sodium carbonate was added all at once so as to absorb immediately all the solution and thus prevent any loss of it by the rapid effervescence which took place on adding the carbonate to the acid perchlorate solution. The carbonate with the absorbed perchlorate could then be mixed easily with a stirring rod. After covering the crucibles tightly, they were heated on a sand bath for several minutes to drive off the excess moisture from the contained carbonates and were gradually heated to bright redness over Bunsen flames. The crucibles and fused mass, while still hot, were plunged into cold water in a beaker, to loosen the mass from the crucible and were heated on the sand bath until the fused substance had completely dissolved. The resulting solutions were then made slightly acid with nitric acid, the chlorine was precipitated with silver nitrate in slight excess, more nitric acid was added, and the solutions were boiled. The silver chloride was filtered, dried and weighed on a Gooch filter. In Table III are given the results obtained, calculated on the basis of the hydrated salt containing two molecules of water of crystallization.

TABLE III.

| No. | Sample taken. Gram. | AgCl found. Gram. | Chlorine found. Per cent. |
|--------|------------------------|----------------------|------------------------------|
| 1..... | 0.1385 | 0.1458 | 26.01 |
| 2..... | 0.1388 | 0.1465 | 26.09 |
| 3..... | 0.1155 | 0.1222 | 26.15 |
| 4..... | 0.0768 | 0.0759 | 26.06 |
| 5..... | 0.0560 | 0.0609 | 26.87 |
| 6..... | 0.1163 | 0.1259 | 26.74 |

Average.....26.32

Theory.....26.36

TABLE IV.

| No. | Sample taken. Gram. | AgCl found. Gram. | Chlorine found. Per cent. |
|--------------|------------------------|----------------------|------------------------------|
| 1..... | 0.0257 | 0.0276 | 30.67 |
| 2..... | 0.0868 | 0.1069 | 30.44 |
| 3..... | 0.0675 | 0.0826 | 30.26 |
| Average..... | | | 30.46 |
| Theory..... | | | 30.44 |

Analyses were also made of the anhydrous salt. These are shown in Table IV.

These results established a formula for hydrazine diperchlorate as $\text{N}_2\text{H}_4 \cdot 2\text{HClO}_4 \cdot 2\text{H}_2\text{O}$.

Hydrazine diperchlorate is not only efflorescent but is also deliquescent. In moist air it takes up water rapidly and dissolves in it. A portion of 0.079 g. exposed to the open air, gained in three and one-half hours 0.48 g. in fifteen and one-half hours, 0.53 g. of absorbed water.

Its solubility is indicated by the following figures determined without

the use of the more refined methods: At 29° , 100 parts of water dissolve 102 parts of the hydrated salt. Solution in water takes place with an absorption of heat. In absolute alcohol, 2.8 parts are soluble in 100 parts of the solvent; in ether, about 1 part is soluble in 100 parts of the solvent. It was not determined whether the salt which crystallized from absolute alcohol was the anhydrous or the hydrated diperchlorate, or the monopерchlorate.

Considerable difficulty was encountered in determining the true melting point of hydrazine diperchlorate. When this operation was conducted in capillary melting point tubes, incipient fusion took place at 95° . But so gradual was the change from the solid to the liquid condition, and so marked was the decomposition before the distinctly molten condition had been reached, that it is not safe to say at what temperature the pure salt actually melts.

Crystalline Structure.—Professor A. C. Gill, of the Department of Geology, Cornell University, has had the very great kindness to make a crystallographic examination of both the mono- and the diperchlorate of hydrazine.

The diperchlorate forms colorless, tabular crystals which are shown by their optical behavior to be orthorhombic.

The acute bisectric emerges exactly normal to the large faces, and extinction is parallel to the longer sides. The substance is optically negative with an optical angle of 30° to $40^{\circ}(?)$ and remarkably strong dispersion of the optical axes.

On attempting to extend and verify these observations two or three weeks later, only crystals of the monacid salt could be found. (As the platinum wire with which they were taken out had also been used with the monacid salt, it is possible that the change may have been in a measure induced by the presence of that compound.) An examination of the crystals of the monopерchlorate showed that they were probably monoclinic. The somewhat elongated tablets showed the oblique emergence of one axis of a negative biaxial interference figure, with large optical angle. The plane of the optical axis is the clinio-pinacoid. Like the diacid compound, the double refraction is strong, but the dispersion is not marked. In the prism zone, the following angles were observed (in the sequence given), starting from the large tabular face: $49^{\circ} 10'$, $57^{\circ} 20'$, $38^{\circ} 50'$, $19^{\circ} 30'$, and $15^{\circ} 10'$.

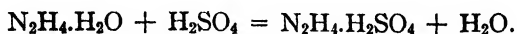
Other Properties.—The diacid salts of hydrazine exhibit strong acid properties. Bach¹ has shown that the dichloride of hydrazine produces the inversion of cane sugar in the same way as does hydrochloric acid in the presence of a chloride. This salt in dilute solutions yields 4 ions.

¹ *Z. physik. Chem.*, 9, 258 (1892).

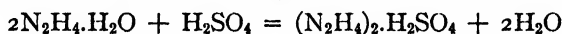
Stolle¹ suggests the use of the disulfate for standardizing solutions of caustic alkalies. On titration, the disalts go over into the monosalts, as indicated by the equation,



Curtius² makes use of this fact to determine titrimetrically hydrazine hydrate with standard sulfuric acid. His statement of the reaction by the equation,



however, is manifestly incorrect, as Stolle's work, as well as numerous titrimetric determinations of hydrazine hydrate in this laboratory, show. The hydrazine disulfate, being largely hydrolyzed in aqueous solution, indicated as the final product in the reaction represented in Curtius's formula, must needs give an acid reaction to indicators. One must, then, necessarily regard this error in the paper of Curtius's as simply an oversight, especially as, when one examines his calculations, it is seen that actually they are not based on this equation, but rather on the equation,



which is the correct one.

In Table V are given the results of a comparison of the methods of Curtius and Rimini when applied to the analysis of anhydrous hydrazine. These analyses were made incidentally in a different research and are used here in substantiation of the preceding statements. The figures in Col. 1 are arrived at from calculations based on Curtius's equation, those in Col. 2, on the corrected equation as given above, and those in Col. 3, are obtained from calculations based on Rimini's iodate method. Each sample of the anhydrous hydrazine served for two analyses. The weighed samples of the anhydrous substance were dissolved in water and titrated with standard acid. On the same solution was then conducted an analysis by the method of Rimini.

TABLE V.

Weight in grams of N_2H_4 found by

| No. | Curtius's method. | | Rimini's method. 3. |
|--------------|-------------------|------------------|------------------------|
| | 1. As stated. | 2. Corrected. | |
| 1..... | 0.030 | 0.060 | 0.061 |
| 2..... | 0.0294 | 0.0588 | 0.0605 |
| 3..... | 0.02998 | 0.0596 | 0.0601 |
| 4..... | 0.0304 | 0.0608 | 0.0597 |
| 5..... | 0.007 | 0.014 | 0.0142 |
| 6..... | 0.012 | 0.024 | 0.0204 |
| 7..... | 0.0298 | 0.0596 | 0.0600 |
| Average..... | 0.02406 | 0.04812 | 0.04799 |

¹ *J. prakt. Chem.*, [2] 66, 332-8 (—).

² *Ibid.*, 42, 521 (1890).

An examination of the hydrazine dichloride, dichlorate and diperchlorate revealed the fact that these salts also are susceptible of titration with solutions of alkali, methyl orange being used as indicator, and of being thereby quantitatively determined, as was shown by Stolle to be the case for the disulfate. Hydrazine diperchlorate also dissolves carbonates with the evolution of carbon dioxide. The dichloride on heating to 180° gives up quantitatively one molecule of its acid,¹ thus resulting in the monochloride. The diperchlorate probably possesses the same property, this surmise being founded on the observation that in a vacuum desiccator and over sulfuric acid the diperchlorate exhibits a marked vapor pressure of perchloric acid, the desiccator becoming filled with the vapor of this acid.

While the pure and dry hydrazine diperchlorate seems to be quite stable, the impure salt, after standing for several months at room temperature, deteriorates, and becomes discolored, assuming a yellow hue. In solution a gradual loss of perchloric acid occurs and crystals of the monoperchlorate form.

The substance, on being struck with a metal hammer, explodes with a loud report.

CORNELL UNIVERSITY, ITHACA, N. Y.

[CONTRIBUTION FROM THE HOSPITAL OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH, NEW YORK.]

A METHOD FOR THE TITRATION OF SMALL AMOUNTS OF HALIDES.

By FRANKLIN C. MCLEAN AND DONALD D. VAN SLYKE.

Received March 5, 1915.

The accuracy, convenience, and wide applicability of the Volhard method for titration of halides has made its use nearly universal. The fact that 1 drop, or about 0.05 cc., of 0.1 *N* solution is required to give the color change satisfactorily at the end point, however, makes it necessary to have under ordinary conditions at least 0.5 milligram molecule of halide, equivalent to 5 cc. of 0.1 *N* silver nitrate, in order that the accuracy of the titration may be within 1%.

The necessity for an accurate means of determining chlorides in small amounts has forced us to seek a titrimetric method with a more sensitive end point, so that less material than is required by the Volhard method may be analyzed with equal percentage accuracy. An iodometric method, with a manipulation almost identical to that of the Volhard titration, proved thoroughly practicable. Like the Volhard, it permits titration in an acid solution, and requires the use only of stable standard solutions, while because of the more sensitive color change it permits one to use

¹ Curtius, *J. prakt. Chem.*, [2] 39, 27 (1889).

0.02 *N* or 0.01 *N* standard solutions and still obtain the end point with one drop. Without sacrificing the accuracy or convenience of the Volhard method, it therefore reduces by about 80% the amount of material required for analysis.

Iodometric determination of chlorides appears to have been first attempted by Pisani,¹ who used a dilute starch-iodine solution to titrate the excess of silver left after precipitation of the chloride with standard silver nitrate solution. Starch-iodine is not stable, however, and consequently the method does not appear to have proven practical. Bang² overcame this disadvantage by utilizing, in place of the starch-iodine, a standard solution of potassium iodide containing a small proportion of potassium iodate. The chloride was precipitated with an excess of standard silver solution containing free nitric acid, the filtrate treated with an excess of the iodide-iodate solution (of about 0.01 *N* conc.), and the excess titrated back with more of the standard silver. A disadvantage of this method is that one can titrate accurately in only one direction; an excess of the iodide-iodate mixture must be added, so that the iodine of all the iodate and of a corresponding amount of iodide is transformed into free iodine ($\text{HIO}_3 + 5\text{HI} = 6\text{I} + 3\text{H}_2\text{O}$). If in titrating one adds the iodine mixture to the silver, the proportion of iodate that is decomposed before the iodide is precipitated depends somewhat on the manner in which the iodine mixture is added, *i. e.*, rate of addition, manner of shaking, etc. It is therefore a drawback that the oxidizing agent used to liberate the iodine of the iodide contains in its own molecule iodine which may also be liberated in the elementary condition. Another drawback to the utilization of the method as described by Bang is the device used to render possible the filtration of the colloidal silver chloride formed in the high dilutions used. The solution containing the precipitate is shaken with kaolin, which adsorbs the silver chloride and gives a clear filtrate. Unfortunately, however, it also adsorbs part of the excess of silver nitrate present. The error introduced by this action was recognized by Bang, who made a correction for it, based on the average amount of silver adsorbed in blank experiments. The necessity for this correction, however, which is not an exact one, makes it impossible to class the method with Volhard's for accuracy. A third disadvantage of Bang's method lies in the titration in the presence of quite concentrated nitric acid, which interferes with the formation of the starch-iodine, and therefore obscures the end point.

The method described below was developed as the result of an attempt to utilize Bang's method. It is similar in principle to the latter (titration with iodide in the presence of an oxidizing agent) but free from the three weaknesses pointed out in the preceding paragraph.

¹ Quoted by Bang, *Biochem. Ztschr.*, 1913, XIX, 33.

² *Loc. cit.*

1. Nitrous, instead of iodic acid, is utilized to free the iodine from the iodide added, so that the possibility of error resulting from incomplete decomposition of iodic acid is eliminated, and one can titrate in either direction. This enables us to simplify the procedure by the elimination of one step, *viz.*: addition of excess of iodide after precipitating the unknown amount of chloride or bromide. As we can now titrate, adding iodide solution to silver, as well as *vice versa*, we need only to filter off the silver bromide or chloride, and titrate the excess of silver in the filtrate directly with standard iodide solution.

2. The use of kaolin or any other adsorbent to make the silver chloride filterable has been rendered unnecessary by utilization of caprylic alcohol to cause coagulation of the colloidal precipitate. This alcohol has a remarkable ability to reduce the surface tension of aqueous solutions, and has been used for some years in this laboratory to prevent foaming of solutions in various operations. Ether has a similar effect of reducing surface tension, although to a less marked extent, and Rothmund and Burgstaller¹ showed that shaking a solution of colloidal silver chloride with ether accelerated the coagulation in the Volhard procedure. Ether did not prove practicable in our case, for its presence interfered with the sensitiveness of the end reaction. Caprylic alcohol, however, is even more efficient, and does not interfere. One adds two or three drops of the alcohol to the solution containing freshly precipitated silver chloride or bromide and shakes vigorously for a few seconds. This treatment coagulates the precipitate to such an extent that it can be collected on an ordinary folded filter, and gives a perfectly clear filtrate. The first few drops that pass through a dry filter are sometimes cloudy, but if they are passed through a second time a clear filtrate is obtained. In fact the filtrates we usually obtained from a silver chloride coagulated with caprylic alcohol were so clear that the turbidity determined with Richard's nephelometer exceeded to a barely detectable degree that of the silver nitrate solution in the dilution used.² In control tests with the nephelometer we could detect 0.1 mg. of NaCl added to a slight excess of silver solution in a liter of water.

3. The addition of a "buffer salt" is utilized in order to give the slight degree of acidity necessary for the sharpest end point. In most cases it is convenient or necessary to precipitate the silver halide in nitric acid solution. When the excess of silver is titrated back with iodide, the presence of free nitric acid in even moderate concentration seriously interferes with the end point. The starch does not, until a considerable excess of iodine is present, combine appreciably with it in strongly acid

¹ *Z. anorg. Chem.*, **63**, 330 (1909).

² Caprylic alcohol can also be used to advantage in gravimetric determination of chlorides to facilitate coagulation of the silver chloride.

solution, and consequently the end point obtained is the yellow-brown color of free iodine, which is much more difficult to detect than the blue of the starch compound. The difficulty is obviated by adding an amount of trisodium citrate, equivalent to the free nitric acid present, before the titration is begun. The amount added may vary 10% above or below an exact equivalent without affecting the end point. A solution containing one molecule of potassium acetate to three of acetic acid may also be used, but the citrate solution appears to give the clearer end point.

Description of the Method.

The halide is precipitated in the presence of a known amount of free nitric acid, preferably about one gram, with an excess of 0.04 *N* or 0.02 *N* standard silver nitrate solution. In the case of bromides and chlorides the silver halide is removed by filtration, after coagulation of the colloid precipitate has been accomplished by shaking the mixture for a few seconds with one or two drops of caprylic alcohol. In case a dry filter is used it may be necessary to pass the first portion of the filtrate through a second time in order to make it perfectly clear.

In either the entire filtrate, washed through the filter, or in an aliquot part, passed through a dry filter, the excess of silver is titrated with 0.02 *N* or 0.01 *N* potassium iodide, which has been standardized against the silver solution.¹ Just before titration one adds from a buret for each gram of free nitric acid present (one gram approximately, or 16 mg. molecules, is contained in 1 cc. of nitric acid of 1.42 specific gravity) 4 cc. of the following solution:

| | | |
|---|------------|---|
| Trisodium citrate, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 5\frac{1}{2}\text{H}_2\text{O}$ | 446.0 g. | { 5/4 gram-molecules or 15/4 equivalents |
| Sodium nitrite..... | 19.0 | |
| Soluble starch..... | 2.5 | |
| Water to..... | 1000.0 cc. | |

One cc. of this solution contains four milligram-equivalents of sodium. The solution, because of its nitrite, serves to liberate iodine; the citrate regulates the acidity of the titrated solution; and the starch is present for the end reaction. Under the above conditions one obtains, with one drop of 0.02 *N* iodide, a very sharp color change, that can be seen in 150 cc. of solution, and is, of course, still more striking in a smaller volume. It is preferable, though not necessary, to keep the volume of the filtrate to be titrated within 50 cc.

The removal, by filtration, of silver chloride or bromide before titrating back with iodide is necessary, because iodine forms a much more insoluble silver salt than either of the other halogens. It reacts with their precipi-

¹ The accuracy of the silver nitrate solution can be checked by titration against 0.01 *N* or 0.02 *N* hydrochloric acid prepared from redistilled acid by the method of Hulett and Bonner, *THIS JOURNAL*, 31, 390 (1909).

tates ($\text{AgCl} + \text{HI} = \text{AgI} + \text{HCl}$) so rapidly that the slight amount of iodine necessary to give the end point is removed from solution in a few seconds by freshly precipitated silver chloride or bromide. This is true for both chlorides and bromides in strongly acid solution. When the acidity is depressed by the addition of sodium citrate as described above, the change still occurs so rapidly with chlorides that no end point with iodide can be obtained. In the case of bromides a sharp end point is obtained that persists for a short time. The amount of iodide necessary to produce this end point is slightly in excess of the correct amount, so that in order to obtain exact results filtration of the bromide precipitate also is necessary (Tables III and IV). When, in either case, the titration is performed after removal of the silver halide precipitate, the end point produced with one drop of excess of iodide lasts for hours, and in fact seems to intensify with time. For reasons similar to the above, *i. e.*, the relative insolubility of silver thiocyanate compared with silver chloride, it is necessary to remove the silver chloride in the Volhard titration in order to obtain the most satisfactory results.¹ Filtration is, of course, unnecessary in the determination of iodides by our method.

Experimental.

Our standard solutions were based on: (1) the constant boiling hydrochloric acid described by Hulett and Bonner² and (2) special "Reagent" metallic silver, which was dissolved in a slight excess of nitric acid. Hulett and Bonner claim a composition constant within one part in 10,000 for the acid distilled by their method, and we have in several years' use of it never found an appreciable variation from their values. The solution used in this case was distilled at 760 mm. atmospheric pressure, so that, according to Hulett and Bonner's table, 180.17 g. contained one gram molecule of HCl .³ The standard solutions made by weight from this acid and from the "Reagent" silver foil checked each other within one part per thousand when titrated by Volhard's method, with filtration of the silver chloride.

The bromide solutions were made by weight from pure potassium bromide, and standardized by careful titration against the silver solution by Volhard's method. As there was no detectible impurity, the salt was not recrystallized.

The potassium iodide solution used was of $M/58.5$ concentration. It was prepared originally for determination of sodium chloride (1 cc. $M/58.5$ $\text{NaCl} = 1$ mg.) and standardized by titration against the silver solutions.

¹ See Rosanoff and Hill, *THIS JOURNAL*, 29, 269 (1907), and Rothmund and Burgstaller, *Z. anorg. Chem.*, 63, 330 (1909).

² *Loc. cit.*

³ Gravimetric determinations gave the following results: 2.1802 g. HCl solution, 1.7350 g. AgCl ; 2.1792 g. HCl , 1.7348 g. AgCl ; g. HCl solution calculated to contain 36.46 g. of HCl , 180.17 and 180.12.

For the determinations of Tables I and III the precipitated and coagulated chloride or bromide was washed several times by decantation, then several times on the filter, with water at room temperature, and the entire filtrate was titrated. For Table II aliquot parts were taken, as indicated.

TABLE I.—DETERMINATIONS ON KNOWN AMOUNTS OF CHLORIDE. TOTAL FILTRATES, WASHED QUANTITATIVELY.

| Cc. HCl. | Cc. AgNO ₃ . | Cc. N/58.5 KI. | Mg. Cl found. | Mg. Cl present. | Error. Mg. Cl. ° | Error. Per cent. |
|------------|-------------------------|----------------|---------------|-----------------|------------------|------------------|
| 1.00 N/50 | 1.00 N/29.25 | 0.82 | 0.715 | 0.709 | +0.006 | +0.8 |
| 1.00 | 1.00 | 0.85 | 0.697 | 0.709 | -0.012 | -1.7 |
| 2.00 | 2.00 | 1.65 | 1.425 | 1.418 | +0.007 | +0.5 |
| 2.00 | 2.00 | 1.66 | 1.418 | 1.418 | 0.000 | 0.0 |
| 5.00 | 5.00 | 4.17 | 3.532 | 3.546 | -0.014 | -0.4 |
| 5.00 | 5.00 | 4.15 | 3.546 | 3.546 | 0.000 | 0.0 |
| 10.00 | 7.00 | 2.30 | 7.092 | 7.092 | 0.000 | 0.0 |
| 10.00 | 7.00 | 2.32 | 7.076 | 7.092 | -0.016 | -0.23 |
| 25.00 | 15.00 | 0.73 | 17.74 | 17.730 | +0.010 | +0.06 |
| 25.00 | 15.00 | 0.80 | 17.70 | 17.730 | -0.030 | -0.17 |
| 20.00 N/14 | 20.00 N/10 | 33.30 | 50.73 | 50.657 | +0.073 | +0.14 |
| 20.00 | 20.00 | 33.40 | 50.67 | 50.657 | +0.013 | +0.025 |
| 20.00 N/10 | 22.00 | 11.83 | 70.84 | 70.920 | -0.079 | -0.11 |
| 20.00 N/10 | 22.00 | 11.82 | 70.85 | 70.920 | -0.073 | -0.10 |

TABLE II.—DETERMINATIONS ON KNOWN AMOUNTS OF CHLORIDE. VOLUME MADE TO 25 CC. FILTERED THROUGH DRY FILTER AND 20 CC. OF FILTRATE TAKEN FOR TITRATION.

| Amt. HCl. | Cc. AgNO ₃ . | Cc. N/58.5 KI. | Mg. Cl found. | Mg. Cl present. | Error. Mg. Cl. | Error. Per cent. |
|------------|-------------------------|----------------|---------------|-----------------|----------------|------------------|
| 1.00 N/50 | 1.00 N/29.5 | 0.68 | 0.697 | 0.709 | -0.008 | -1.1 |
| 1.00 | 1.00 | 0.70 | 0.688 | 0.709 | -0.021 | -3.0 |
| 5.00 | 5.00 | 3.35 | 3.521 | 3.546 | -0.025 | -0.7 |
| 5.00 | 5.00 | 3.31 | 3.555 | 3.546 | +0.007 | +0.2 |
| 10.00 | 7.00 | 1.85 | 7.086 | 7.092 | -0.006 | -0.08 |
| 10.00 | 7.00 | 1.82 | 7.014 | 7.092 | +0.012 | +0.17 |
| 20.00 N/10 | 21.00 N/10 | 5.98 | 70.82 | 70.92 | -0.10 | -0.14 |
| 20.00 | 22.00 | 11.53 | 71.02 | 70.92 | +0.10 | +0.13 |

TABLE III.—DETERMINATIONS ON KNOWN AMOUNTS OF BROMIDE. TOTAL FILTRATES, WASHED QUANTITATIVELY.

Solution of KBr. 1 cc. = 0.994 Mg. KBr and 0.667 Mg. Br.

| Cc. of KBr sol. | Cc. AgNO ₃ . | Cc. N/58.5 KI. | Mg. Br found. | Mg. Br present. | Error. Mg. Br. | Error. Per cent. |
|-----------------|-------------------------|----------------|---------------|-----------------|----------------|------------------|
| 4.000 | 2.00 N/29.25 | 2.04 | 2.675 | 2.668 | +0.007 | +0.26 |
| 4.000 | 2.00 | 2.00 | 2.730 | 2.668 | +0.062 | +2.3 |
| 5.000 | 2.00 | 1.55 | 3.345 | 3.335 | +0.010 | +0.3 |
| 5.000 | 2.00 | 1.55 | 3.345 | 3.335 | +0.010 | +0.3 |
| 7.000 | 3.00 | 2.60 | 4.640 | 4.669 | -0.029 | -0.62 |
| 7.000 | 3.00 | 2.62 | 4.613 | 4.669 | -0.056 | -1.20 |
| 25.000 | 7.00 | 1.73 | 16.74 | 16.69 | +0.05 | +0.30 |
| 25.000 | 7.00 | 1.75 | 16.72 | 16.69 | +0.03 | +0.18 |
| 50.174 | 5.00 N/10 | 4.78 | 33.43 | 33.43 | 0.000 | =0.00 |
| 50.174 | 5.00 | 4.75 | 33.47 | 33.43 | +0.04 | +0.11 |

In the bromide determinations of Table IV the silver bromide was not filtered off, and the iodide titration was performed in its presence. It will be seen that under these conditions an error of 1-2% must be allowed for, because of the reaction between HI and AgBr already discussed.

TABLE IV.—DETERMINATIONS ON KNOWN AMOUNTS OF BROMIDE. TITRATION PERFORMED IN PRESENCE OF AgBr PRECIPITATE.

| Cc. KBr solution (1 cc. = 0.667 mg. Br). | * Cc. N/29.25 AgNO ₃ . | Cc. N/58.5 KI. | Mg. Br found. | Mg. Br present. | Error, Mg. Br. | Error, Per cent. |
|--|-----------------------------------|----------------|---------------|-----------------|----------------|------------------|
| 4.00 | 2.00 | 2.08 | 2.620 | 2.668 | -0.048 | -1.8 |
| 4.00 | 2.00 | 2.10 | 2.593 | 2.668 | -0.075 | -2.8 |
| 5.00 | 2.00 | 1.58 | 3.305 | 3.335 | -0.030 | -0.9 |
| 5.00 | 2.00 | 1.58 | 3.305 | 3.335 | -0.030 | -0.9 |
| 10.00 | 4.00 | 3.18 | 6.580 | 6.670 | -0.090 | -1.35 |
| 10.00 | 4.00 | 3.20 | 6.555 | 6.670 | -0.115 | -1.70 |
| 25.00 | 7.00 | 2.10 | 16.250 | 16.690 | -0.440 | -2.6 |
| 25.00 | 7.00 | 1.92 | 16.500 | 16.690 | -0.190 | -1.1 |

From inspection of Tables I, II and III it will be seen that the titration error exceeds 0.05 cc. (1 drop) of the *M*/58.5 KI solution, equivalent to 0.03 mg. Cl or 0.07 mg. Br, only when the amounts titrated are so large that this error falls within or near the 1 pro mille limit. In most cases where small amounts were analyzed, the results indicate that the absolute error was within half a drop.

The percentage error ranges from a maximum of 3% in analyses of the smallest amounts, 0.7 mg. Cl and 2.6 mg. Br, down to 0.1% towards the other end of the scale, where amounts up to 70 mg. of Cl and 33 mg. of Br were determined.

Summary.

A method for titration of halides is described which permits utilization of the starch-iodine color for the end point. Because of the sensitiveness of the color change under the conditions ascertained, and the simplicity of the manipulation, amounts of halide no greater than 0.5 mg. molecule can be determined with an accuracy of one part per thousand.

THE OXIDATION OF SULFIDES WITH POTASSIUM IODATE.

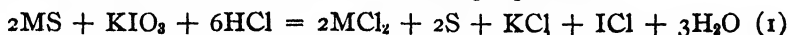
By REGINALD S. DEAN.

Received February 22, 1915.

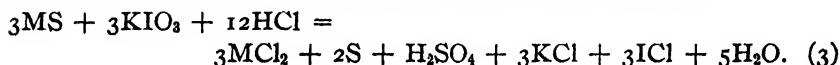
L. W. Andrews¹ has shown that in solutions containing 50% by volume, or more, of concentrated hydrochloric acid at the end of the titration, potassium iodate may be used as an oxidizing agent, and that under such conditions the iodine, which is at first liberated by the reduction of iodate, is finally completely converted into iodine chloride, ICl, and the end of the titration can be shown by the disappearance of the iodine color in

¹ THIS JOURNAL, 25, 756 (1903).

some chloroform which is mixed with the liquid to be titrated. This method has been applied to the determination of copper,¹ antimony,² mercury,³ hydrazine⁴ and lead peroxide.⁵ Not the least striking of the advantages of the method is its applicability in the presence of solid material and organic matter such as filter paper. This made it seem not improbable that the method could be extended to the determination of sulfides, especially where the sulfide is easily washed without oxidation, as is the case with arsenic and antimony. We would expect the reaction to proceed according to one of the following equations:



we have found that the amount of iodate solution required for the oxidation of cadmium, zinc and lead sulfides does not correspond to either of these equations, but instead, $\frac{1}{3}$ of the sulfur is oxidized to sulfuric acid, while $\frac{2}{3}$ is liberated as free sulfur in accordance with the equation



When a smaller proportion of hydrochloric acid is present, however, the amount of iodate corresponds more nearly to the first equation.

Experimental.

(a) **Cadmium.**—Cadmium sulfide was chosen to work with since it is comparatively easy to wash without oxidation and is easily soluble in hydrochloric acid. Ten cc. of 0.1 molar cadmium sulfate solution was precipitated with H_2S , the precipitated sulfide was filtered and washed free from H_2S and then the filter and contents were placed in a bottle containing nearly the required amount of iodate and hydrochloric acid. The liberated iodine was titrated with iodate, using chloroform or carbon tetrachloride as indicator. If an excess of iodate was used it was titrated back with standard iodide. The results were as follows:

Cadmium sulfide used was 0.144 g. = 1 millimol.

| | | | | | | | | |
|--|------|------|------|------|------|------|------|------|
| Concentration of HCl (% by vol.) | 10 | 15 | 30 | 40 | 75 | 75 | 75 | 80 |
| Cc. 0.05 M KIO ₃ | 10 | 10.1 | 14.2 | 17.5 | 19.8 | 20.0 | 20.1 | 19.9 |
| Concentration of HCl (% by vol.) | 80 | 96 | | | | | | |
| Cc. 0.2 M KIO ₃ | 4.95 | 5.00 | | | | | | |

The acid concentrations are calculated on the volume after titration.

From the above results we see that, in solutions containing 10–15% concentrated acid, the reaction proceeds as represented in Equation 1; below this concentration difficulties are encountered in dissolving the sulfide

¹ Jamieson, Levi and Wells, *THIS JOURNAL*, 30, 760 (1908).

² Jamieson, *J. Ind. Eng. Chem.*, 3, 250 (1911).

³ Jamieson, *Am. J. Sci.*, 33, 349 (1912).

⁴ Jamieson, *Ibid.*, 33, 349 (1912).

⁵ R. S. Dean, *Chem. News*, 111, 2 (1915).

and in the hydrolysis of the iodine chloride; with increasing concentration of acid, the consumption of iodate increases and reaches a maximum when the ratio of iodate to sulfide is 1:1, as represented by Equation 3, according to which only one-third of the sulfur is oxidized to sulfuric acid.

In order to test this last assumption, four solutions from the above titrations, two of 75% acid, and one each of 80% and 96% acid, were filtered from the filter paper, sulfur, etc., and, after boiling off the HCl and ICl, were precipitated with barium chloride, the barium sulfate being weighed and calculated to sulfur. The results were as follows:

Cadmium sulfide used = 0.1444 g. = 0.0321 g. sulfur.

| | | | | |
|--|--------|--------|--------|--------|
| Concentration of HCl (% by vol.). | 75 | 75 | 80 | 96 |
| Sulfur found as H ₂ SO ₄ | 0.0106 | 0.0110 | 0.0103 | 0.0109 |

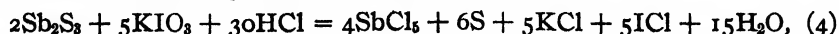
It will be noticed that the sulfur oxidized to H₂SO₄ is, within the experimental error, exactly one-third of the total sulfur.

(b) **Zinc.**—We would expect zinc sulfide to oxidize exactly as the cadmium and we find that such is the case; only two concentrations of acid were used. The zinc was precipitated from a formic acid solution and treated exactly as the cadmium. The zinc solution used was of such strength that, oxidizing according to Equation 1, 25 cc. of 0.05 molar iodate would be required, while oxidizing according to Equation 3, 50 cc. would be required. The results were:

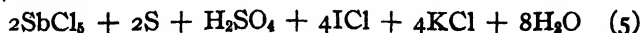
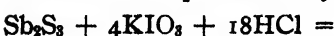
| | | | | | | | |
|--------------------------------------|------|------|------|------|------|------|------|
| Concentration of HCl (% by vol.).... | 15 | 15 | 15 | 65 | 65 | 65 | 65 |
| Cc. 0.05 M iodate..... | 25.4 | 25.2 | 24.8 | 49.8 | 50.2 | 50.5 | 49.8 |

(c) **Lead.**—Lead sulfide was precipitated from a solution of known strength, filtered, washed, and titrated in the same manner as the zinc and cadmium. The concentration of acid used was about 75%. The sulfide was of such an amount that if oxidized according to Equation 3, 24.0 cc. of 0.05 M iodate would be required. The results were 23.9, 24.0, 24.0, 24.2, respectively.

(d) **Antimony.**—Antimony was chosen as a representative of the sulfides, in which the metal shows two states of oxidation. From our work on cadmium we would expect that antimony would be oxidized at low concentrations according to the equation



while with increasing concentration it would approach and finally reach the reaction represented by the following equation:



That the above gives the correct ratio is shown by the following results:

The antimony was precipitated from 10 cc. of a 0.1 molar solution of potassium-antimonyl tartrate and treated exactly as was the cadmium; the reaction proceeding according to Equation 4. would require 25 cc.

0.05 molar iodate while according to (5) it would require 40 cc. The results were as follows:

| | | | | | | | | |
|-----------------------------------|------|------|------|------|------|------|------|------|
| Conc. of HCl (% by vol.)..... | 26 | 31 | 36 | 40 | 60 | 65 | 70 | 90 |
| Cc. 0.05 M KIO ₃ | 26.2 | 28.2 | 29.6 | 32.2 | 40.4 | 39.9 | 40.2 | 40.0 |

The above results show, as with the cadmium, that with maximum oxidation only one-third of the sulfur is oxidized to sulfuric acid; they do not show the minimum found with cadmium, as the insolubility of antimony sulfide makes it inconvenient to work in the less concentrated solution.

(e) **Arsenic.**—As L. W. Andrews explicitly states, with higher concentrations of hydrochloric acid no oxidation of arsenic takes place. We would naturally predict then that only the sulfur from the arsenious sulfide would be oxidized, thus:



The results with arsenious sulfide showed, however, only $\frac{2}{3}$ of the iodate called for by this equation; no satisfactory explanation has been found for this result.

10 cc. of an 0.08 M solution of arsenious chloride was precipitated as sulfide and titrated with 0.05 M iodate with about 80% concentrated acid. The iodate required according to Equation 6 would be 24.0 cc. The iodate consumed was 16.0, 16.0, 16.3, 16.0, respectively. Whether this apparently exact ratio of 2 iodate to 1 arsenic sulfide is accidental or not we have not determined, because the insolubility of the sulfide limits the applicable concentration to practically pure acid.

This work was done under the direction of Prof. U. H. Gottschalk.

MISSOURI SCHOOL OF MINES,
ROLLA, MO.

THE DETERMINATION OF BORON IN IRON.

By J. M. LINDGREN.

Received March 12, 1915.

The present work has had to deal with the determination of small percentages of boron in iron. Two procedures have been tried. First, the well-known method of Gooch,¹ which consists in the formation of methyl borate and distillation of the ester in a properly arranged apparatus, with recovery of the boron in the form of calcium borate. The complications involved in this method are accentuated by reason of the large quantity of iron oxide and the fact that distillation must be repeated at least six times.

The other method made use of is that proposed by Wherry² which involves titration with alkali of the boric acid in the filtrate obtained

¹ *Am. Chem. J.*, 9, 23 (1887).

² *THIS JOURNAL*, 30, 1687 (1908).

after precipitating the iron. The application of this method to the present problem made it necessary to determine whether it is possible to recover the relatively small amounts of boric acid in the presence of large amounts of ferric hydroxide. After considerable experimentation this was found to be entirely feasible without departing in any marked degree from the principles involved in the method as set forth by Wherry. The details of the procedure are as follows:

Two to three grams of iron are dissolved in a round-bottomed Jena flask of about 800 cc. capacity, using 10 cc. each of nitric acid (sp. gr. 1.4), hydrochloric acid (sp. gr. 1.2), and water. When the action is completed the solution is cooled to room temperature and the iron precipitated by use of C. P. calcium carbonate. If not properly carried out this precipitation may result in the formation of colloidal hydrate. It will be noted that the volume of the solution is approximately 30 cc. If to this solution there is added, all at one time, approximately double the amount of dry calcium carbonate necessary for complete neutralization, and the mixture is stirred by vigorous agitation, a pasty or solid mass results, which, upon the addition of hot water, yields ferric hydroxide in the form of a dark brown and very granular precipitate. Two hundred and fifty to three hundred cc. of carbon-dioxide-free water are added and the mixture is boiled under a reflux condenser for at least 30 minutes to assure entire absence of carbon dioxide or bicarbonate.

Before filtering, and in order to still further open up the precipitate to admit of thorough washing, there is now added a considerable quantity of asbestos fiber which has been well washed. A good method for preparing the asbestos is to digest over night on the steam bath a considerable quantity in dilute hydrochloric acid. This should be well washed and suspended in boiling water. The fiber is added wet to the precipitated iron, the amount needed in each process being approximately 50 cc. in bulk, sufficient to thoroughly impregnate the precipitated iron. After boiling the mixture for a few minutes the precipitate is filtered at once by suction through a Büchner funnel, about 15 cm. in diameter, having a double thickness of filter paper carefully fitted over the bottom. A splash trap is connected to the receiving flask. The precipitate should be washed 8 or 10 times with boiling hot water. The funnel is then removed and replaced by a solid rubber stopper. By renewal of the suction, further ebullition is produced in the flask without addition of more heat. The solution is then cooled and titrated as follows with 0.1 *N* alkali (free from carbonate). After addition of a few drops of phenolphthalein, alkali is added until a pink color appears. One gram of mannite is next added, and the titration continued until a permanent pink color is obtained.¹ Familiarity with the end point is attained by practice. A blank should

¹ For details of the reactions see *THIS JOURNAL*, 30, 1699 (1908).

be carried through using pure iron and following the process exactly as described.

In testing the accuracy of the method, 0.1 *N* solution of boron was prepared by dissolving 3.5 g. of B_2O_3 in one liter of CO_2 -free water. The B_2O_3 was prepared by fusing pure boric acid in a platinum dish. When titrated in the presence of mannite, 8.68 cc. of this B_2O_3 solution required 8.75 cc. 0.1 *N* KOH. Known quantities of this boric acid solution were added to a solution of iron free from boron and the operations were carried out as indicated. Contrary to the experience of Wherry, when the precipitation by use of calcium carbonate was properly carried out, it was found possible to wash the iron entirely free from boric acid and recover the full amount in the filtrate. The use of the boric acid solution made up of the pure fused material as above described also served admirably as a medium for standardizing the alkali used in the titrations.

TABLE I.—DETERMINATION OF BORON IN IRON.

| | | | | |
|--------------------|-------|-------|-------|-------|
| % Boron taken..... | 0.038 | 0.188 | 0.424 | 0.850 |
| % Boron found..... | 0.044 | 0.194 | 0.388 | 0.840 |

URBANA, ILL.

CHEMICAL REACTIONS AT LOW PRESSURES.¹

By IRVING LANGMUIR.

Received March 31, 1915.

In the course of investigations into the causes of the blackening of tungsten lamps,² the effects produced by the introduction of low pressures of various gases have been studied in considerable detail.

It had been previously known³ that the vacuum in a lighted tungsten lamp normally improves during the life of the lamp, but it was thought that this removal of the residual gases⁴ was brought about by electrical discharges in much the same way as that commonly observed in Geissler and Roentgen ray tubes. These experiments have shown, however, that a highly heated tungsten filament will cause the disappearance or clean-up of nearly any gas introduced into the bulb at low pressure, and that this action, in the great majority of cases, is purely chemical in nature.

The experimental methods that have been employed in these investigations are relatively simple. A bulb containing one or more short filaments, usually of tungsten, was sealed to an apparatus consisting essentially of a mercury Gaede pump, a sensitive McLeod gage for reading the pressures, and an apparatus for introducing small quantities of various

¹ Paper presented before the New York Section of the American Chemical Society, March 5, 1915.

² *Trans. A. I. E. E.*, **32**, 1913 (1913).

³ *This Journal*, **35**, 107 (1913).

gases into the system and for analyzing the gas residues obtained in the course of the experiments.

By means of the pump, the pressure in the system could be lowered to 0.00002 mm. of mercury. The McLeod gage gave a reading of one millimeter on the scale for a pressure of 0.000007 mm. of mercury. By means of the apparatus for analyzing gas, a quantitative analysis of a single cubic mm. (at atmospheric pressure) of gas could be carried out, determining the following constituents: hydrogen, oxygen, carbon dioxide, carbon monoxide, nitrogen and the inert gases.

The apparatus by which this has been accomplished has been in almost daily use for over five years, and during that time a very large number of reactions have been studied by its aid. In a typical experiment, after having thoroughly exhausted the whole apparatus, a small quantity, usually 5-20 mm. of gas, is introduced and the filament is electrically heated to a definite temperature, while readings of the pressure are taken at regular intervals (usually one minute). By plotting the pressure readings against the time, a curve is obtained which clearly shows how the rate of clean-up varies with the pressure.

A series of such curves are prepared with different filament temperatures and with various other changes in the conditions which I shall describe later.

In this way we have studied the clean-up phenomena with many different gases and several different kinds of filaments. Most of the work has been done with tungsten filaments, but, in order to get a broader outlook over the field of low-pressure reactions, filaments of carbon, molybdenum, platinum, iron, palladium, and other metals have also been tried. The principal gases studied have been oxygen, nitrogen, hydrogen, carbon monoxide and dioxide, chlorine, bromine, iodine, methane, cyanogen, hydrochloric acid, argon, phosphine, and the vapors of many substances, such as mercury, phosphorus pentoxide, sulfur, etc.

With each of these gases, conditions can be found, under which a heated tungsten filament will cause the clean-up of the gas. The curves obtained in the course of the experiments have furnished very complete data for a study of the kinetics of the reactions involved.

It has long been generally recognized that the kinetics of gas reactions afford the best, if not the only means of studying the mechanism of reactions, and the literature of recent years shows that the velocities of many reactions have been investigated with this end in view.

Very few experimenters, however, have realized that by working with gases at extremely low pressures the experimental conditions may be enormously simplified and the velocity of the reaction is then much more intimately related to the behavior of the individual molecule than it is at higher pressures.

In fact, by working continually with gases at these low pressures, one soon acquires an entirely new view-point and sees almost daily fresh evidences of the atomic and molecular structure of matter. The kinetic theory of gases then becomes the great guiding principle. According to this view-point, the velocity of a reaction is a matter of statistics. The question becomes: Out of all the gas molecules which strike the surface of heated filament, what fraction enter into reaction with it?

This statistical view-point has become prevalent among physicists within the last few years. Without it, the tremendous advances in our knowledge of radioactivity, electric conduction through gases, applications of the quantum theory, etc., would have been impossible.

In the field of chemistry, however, only a very small beginning has been made. Chemistry was the first of the sciences to make use of the atomic theory, and, in fact, the history of chemistry in the last century shows that the great advances in both inorganic and organic chemistry were largely dependent on this theory.

The development of physical chemistry, however, took place along rather different lines. The remarkable progress which occurred from 1870 to 1900 was, in a large degree, based upon the applications of thermodynamics to chemistry. Gradually, the idea became prevalent that the atomic theory was only a working hypothesis and might perhaps profitably be dispensed with entirely. The energy relations of reactions, on the other hand, were considered to be of the most fundamental importance. Just about the time that the majority of physical chemists had been won over to this view-point the physicists began to discover absolute proofs of the existence of atoms and molecules and soon showed what remarkable results could be obtained by the applications of statistical methods.

As yet, apparently, very few chemists have awakened to the wonderful opportunities that lie open to them on all sides when they attack the problems of chemistry by the new methods which the physicists have developed. The physicist, on the other hand, is gradually beginning to extend his investigations into the field of the chemist and we may hope, if the chemist will but meet him half way, that there will result a new physical chemistry which will have an even more, far-reaching effect on our ordinary chemical conceptions than has the physical chemistry of the last decades.

Perhaps the most noteworthy of the recent attempts to apply statistical methods to chemical changes is the work of J. J. Thomson on positive rays.

Strutt¹ has studied the statistics of a few gas reactions, in some of which his active modification of nitrogen (atomic nitrogen) takes part. Although his experimental methods are quite different from those we have

¹ *Proc. Roy. Soc., (A)* 87, 302 (1912).

used in studying the clean-up of gases, his results are closely related to some of those we have obtained, and I shall therefore have occasion to refer again to this work of Strutt's.

An excellent example of the study of chemical reactions, by statistical methods, and this time by a chemist, is to be found in the work of S. C. Lind¹ on the nature of chemical action brought about by radioactive bodies.

The reactions which we are to consider this evening are for the most part reactions between gases and heated filaments; that is, they are heterogeneous reactions involving a solid and gaseous phase. The kinetics of reactions of this type have not received the attention which has been accorded to homogeneous reactions. For example, in Jellinek's recent book on the "Physical Chemistry of Gas Reactions," 34 pages are devoted to the kinetics of homogeneous reactions, but only half of one page to the kinetics of heterogeneous reactions.

It was at first thought that the law of mass action could be applied to heterogeneous reactions just as to homogeneous reactions. Experiments soon showed, however, that other factors than purely chemical ones usually determined the velocity of these reactions. Noyes and Whitney² studied the rate of solution of solid substances in liquids and concluded that the velocity was dependent entirely on the rate at which the dissolved substances could diffuse out through the thin layer of liquid next to the solid. Stirring the liquid had the effect of thinning this layer and so increased the rate.

Nernst extended this idea and suggested that the velocity of heterogeneous reactions in general was limited by the rate of diffusion of the reacting substances through a "diffusion layer," which he considered, under ordinary circumstances, to be of constant thickness. Thus he reasoned that the velocity of these reactions, in practically all cases, should be proportional to the concentration of the reacting substances. In other words, the reactions should follow the laws of monomolecular reactions. Nernst pointed out, however, that it was wrong to draw conclusions as to the mechanism of heterogeneous reactions from measurements of their velocity.

Fink,³ as a result of his study of the kinetics of the sulfur trioxide contact process, developed a theory of the mechanism which marked a new step in our conceptions of the mechanism of heterogeneous reactions. Bodenstein and Fink⁴ successfully applied this theory to a large number of other catalytic reactions.

¹ *J. Phys. Chem.*, **16**, 564 (1912).

² *Z. physik. Chem.*, **23**, 689 (1897).

³ *Dissertation*, Leipzig, 1907; see also Bodenstein and Fink, *Z. physik. Chem.*, **60**, 1 (1907).

⁴ *Z. physik. Chem.*, **60**, 46 (1907).

This theory differs essentially from Nernst's, in that the reaction velocity is assumed to be limited by the rate of diffusion of the reacting bodies through an *adsorbed film of variable thickness*. Thus, in the case of the reaction



in contact with platinum it is shown that there is present on the platinum an adsorbed layer of SO_3 . The theory assumes that the thickness of this layer is at all times proportional to the square root of the concentration of SO_3 in the gas phase; in other words, that there is an adsorption equilibrium. The reaction is assumed to take place only at the boundary between the adsorption film and the platinum. The oxygen and sulfur dioxide must therefore diffuse through the film before being able to react. In this way the theory indicates that the velocity of the reaction should be inversely proportional to the square root of the concentration of SO_3 and should be proportional either to the concentration of oxygen or to that of the sulfur dioxide (not to both), depending upon which is in excess at the surface of the platinum.

This theory seems to have met with general favor and has been applied to the kinetics of many heterogeneous reactions.

The experiments on gas reactions at low pressures which I shall describe this evening, have shown that this theory must be modified and that we must consider the reaction velocity to be limited, not by the rate of diffusion through the adsorbed film, but rather, by the rate at which the surface of the metal becomes exposed by the evaporation of single molecules from an adsorbed layer one molecule deep. We shall see that the statistical view-point will lead us very much further in the understanding of all reactions of this type.

In interpreting the experimental results, we shall need to make use of some of the fundamental principles of the kinetic theory. I should therefore like to spend some time in discussing these and in showing their relation to the phenomena we shall have to consider.

We shall refer frequently to low gas pressures, and it will be well at the outset to say a word as to the unit of pressure which we shall use throughout. It has been customary to measure pressures in mm. of mercury, but this is really a very arbitrary and inconvenient unit for such work as this. Professor Richards, last year at Cincinnati, made a strong appeal to chemists to use the C. G. S. unit of pressure, the *bar*, or the megabar, and enumerated many good reasons for doing so. The *bar* is defined as a pressure of one dyne per sq. cm. and the megabar is a million times this. The megabar is almost exactly 750 mm. of mercury and is really more nearly average atmospheric pressure than the 760 mm. usually adopted as standard. A bar is therefore one millionth of an atmosphere, or just three-fourths of a thousandth of a mm. of mercury.

This unit is particularly convenient for our purpose, for the pressures we shall deal with are usually from 1 to 100 bars.

According to the kinetic theory, the pressure of a gas on the walls of the containing vessel is due to the impact of the rapidly moving molecules against the surface. The average velocity (Ω) of the molecules is

$$\Omega = \sqrt{8RT/\pi M} \quad (1)$$

where T is the absolute temperature, M the molecular weight, and R the gas constant (83.2×10^6 ergs/degree). If we substitute the numerical value of R in this equation we find

$$\Omega = 14550 \sqrt{T/M} \text{ cm. per sec.} \quad (2)$$

We see that the velocity is proportional to the square root of the temperature and inversely proportional to the square root of the molecular weight. For oxygen at room temperature ($T = 293$; $M = 32$), the average velocity of the molecule is 44000 cm. per second, or nearly half a kilometer per second (about 30% greater than the velocity of sound). The pressure of the gas being produced by the impact of the molecules, is proportional to the velocity of the molecules as given above and also to the total mass of all the molecules striking the surface per second. If we let m represent the number of grams of gas molecules which strike a unit surface per second, then it can be shown that the pressure p is equal to

$$p = \frac{1}{2} \pi m \Omega. \quad (3)$$

From this and (1), we find m to be

$$m = \sqrt{M/2\pi RT} p. \quad (4)$$

We shall find that this is an equation of very fundamental importance in the theory of the kinetics of heterogeneous reactions. It enables us to calculate the exact rate at which the gas can come into contact with a given surface. Substituting the numerical value of R , etc., the equation becomes

$$m = 43.74 \times 10^{-6} \sqrt{M/T} p. \quad (5)$$

Here m is expressed in grams per sq. cm. per second and p is in bars.

For air ($M = 29$) at atmospheric pressure (10^6 bars) and room temperature ($T = 293$), this gives $m = 13.8$ g. per sq. cm. per second. This mass of air corresponds to about twelve liters.

Let us pause a moment to consider what this means. In each second, the total number of molecules striking a single sq. cm. of surface is as great as is the number contained in twelve liters of air. Of course, under ordinary conditions, the same molecules strike the surface a vast number of times each second. As the pressure is lowered, the number of molecules striking the surface decreases, but so does the number contained in a given volume. Thus we see that no matter what the pressure, the number of molecules which strike a single square centimeter of surface in a second is the same as that contained in twelve liters.

According to Millikan's recent accurate determinations, there are 2.488×10^{19} molecules in a cubic centimeter of any gas at 20°C . and one megabar pressure. The lowest pressures that have been produced and measured are about 0.001 bar, or 10^{-9} megabars. Even in this remarkably good vacuum, there are still 2.5×10^{10} molecules per cubic centimeter. However, when we consider that the average distance between the molecules under these conditions is about 0.02 mm., a distance about equal to the diameter of the filament of a small tungsten lamp, we realize that the gas must behave very differently from a continuous medium.

For many calculations the number of molecules per g. molecule is a very convenient number. According to Millikan's data, this is 6.062×10^{23} . For example, from this figure we can calculate (by Equation 5) the number of molecules of a gas which strike a sq. cm. of surface per second. We find this number to be

$$n = 2.652 \times 10^{19} p / \sqrt{MT}. \quad (6)$$

Very little is known about the diameter of molecules. The question itself probably has little meaning, for molecules are certainly not spheres, but are complex structures of electrons having no definite geometrical shape which can be adequately characterized by a single dimension. We do know, accurately, however, the distances between adjacent molecules in crystals, and in gases we know approximately how close the centers of molecules can approach during collisions. For oxygen, this distance, which, for convenience, we may call the diameter, has been found to be 2.7×10^{-8} cm. If we assume that these molecules are arranged in a single layer on a surface, much as the cells in honeycomb are arranged, it can be readily shown that the total number required to cover a square centimeter is 1.6×10^{15} .

The area covered by each molecule is the reciprocal of this, or 6×10^{-16} sq. cm. We already know, by Equation 6, how many molecules strike a sq. cm. per second, so to find how many molecules from the gas strike a given molecule on the surface we need only to multiply by 6×10^{-16} . We thus find, for the case of oxygen at room temperature and at a pressure of one bar, that an oxygen molecule on the surface would be struck by 170 molecules from the gas every second. Similarly, if the surface were originally free from oxygen and every oxygen molecule striking the surface should stick, it would take approximately only $1/170$ of a second to cover the surface with a layer one molecule deep. Even at 0.001 bar pressure, the lowest pressure that has been measured, it would require only about 6 seconds to form such a film. This explains the difficulty of preparing surfaces in vacuum which are not contaminated by gas.

A very fundamental conception is that of evaporation. By means of Equation 4 we may obtain a relation between the vapor pressure of a substance and its rate of evaporation. When a substance is in equilibrium

with its saturated vapor the vapor is condensing on the substance at the same rate as the latter is evaporating. Now if we assume that every molecule of the vapor striking the surface condenses, then Equation 4 gives us the rate (m) at which the vapor must condense. This must be equal to the rate at which the substance evaporates.

Let us now consider the essential differences between the conditions in our low pressure experiments and those that would prevail if higher pressures were used.

At pressures as high as atmospheric pressure, convection currents set up by the filament introduce very serious complications. At pressures of a tenth of a megabar or less, convection currents become negligible for most purposes, but the problem is still complicated by the sharp temperature gradients that occur in the gas around the wire. At ordinary pressures, unless the velocity of the reaction is extremely small, the rate of reaction will be determined largely, if not wholly, by the rate at which the reacting substances can diffuse to the surface and the products diffuse out. Under these circumstances, we should expect Nernst's theory to apply in general, but in this case we are really not measuring the velocity of a chemical reaction at all; we are merely measuring a diffusion coefficient in a gas.

On the other hand, at pressures as low as 10 bars, diffusion may be considered as practically infinitely rapid. At this pressure the average free path of the molecules of most gases is very close to 1 cm. This is so large, compared to the diameter of the wire, that it is evident that the molecules leaving the wire can in no way interfere with those approaching it. Under these conditions the gases don't need to diffuse through each other in the ordinary way.

At such low pressures as these we may, in fact, look upon the gas as consisting of a swarm of molecules which are independent of one another. The velocity of the molecules around the filament is then determined by the temperature of the bulb and is entirely independent of that of the filament. There is thus no temperature gradient in the gas around the filament. The average velocity of the molecules striking the filament is definitely known and, in case two or more gases are present, the relative numbers of each kind of molecules striking the filament are also known, no matter how rapid the reaction may be.

An interesting feature, possible only with reactions at very low pressures, is the fact that the temperature of the molecules striking the filament is different from that of the filament itself. At ordinary pressures, because of the heat conductivity of the gas, the molecules striking a solid body are, of course, always at the same temperature as the body itself. This opens up new possibilities in studying the kinetics of reactions. The effect of separate variation in the temperature of two reacting sub-

stances can thus be studied. If it is the impact of the gas molecules against the surface of the filament which determines the velocity of the reaction, then this velocity should depend much more on the temperature of the bulb than on that of the filament, since the impact depends on relative velocity, and the velocity of the heavy tungsten atoms, even at high temperatures, is much less than that of ordinary gas molecules at room temperature. On the other hand, if the reaction velocity is determined rather by some condition of the surface of the filament, then the effect of bulb temperature will usually be negligible.

Another result of the use of low pressures is that the molecules of the products of a reaction, when they leave the filament, do not return again until after having made many collisions with the bulb. If the substance formed is a nonvolatile solid, or can be condensed by cooling the bulb in liquid air, it is thus possible to make certain that the reaction does not take place as the result of two collisions, but necessarily occurs in one. In this way also it should be possible to produce many compounds which are very unstable at the temperature of the filament.

At sufficiently low pressures (about 1 or 2 bars) the molecules leaving the filament travel directly to the bulb without striking any other molecules on the way. Naturally, they have no chance of giving up any energy on the way to the bulb, and therefore (if we can speak of the temperature of a single molecule) reach the bulb with the same temperature as that with which they left the filament. This must produce the most sudden cooling possible, and there is then the minimum chance for the decomposition of the product formed if it happens to be unstable at some temperature between that of the filament and that of the bulb.

Another important advantage in working at low pressures is that the velocity of even the most rapid reactions in this way can be slowed down sufficiently so that they can be studied quantitatively. The heat liberated by the reaction on the filament is usually so small that it is not noticeable, or at any rate is not so large but that isothermal conditions may be maintained.

The theories of the mechanism of reactions that I will describe in connection with the experiments have been gradually developed during the last three or four years. To-night I shall discuss only the purely chemical evidence, but I should like to point out that the idea that the reaction velocity depends not upon the thickness of the adsorption layer, but upon the extent to which the surface is covered by it, was based upon experiments on the electron emission from heated tungsten wires in high vacuum. The evidence of the existence of such monomolecular layers in these experiments was very striking and the electron emission was found to depend entirely upon the extent of the uncovered part of the

surface. A preliminary account of this work was published in 1913.¹ I expect later to publish the results of the more recent experiments and to show that in the measurement of the electron emission from heated wires there is opened up a powerful method of studying the properties of films so thin that they only partly cover the surface with a layer one molecule deep.

We are now in a position to consider more in detail the reactions which occur when a gas is "cleaned-up" by a heated filament. These reactions may be divided into four distinct classes, which we shall consider separately. The four types of reaction are those in which:

1. The filament is attacked by the gas.
2. The gas reacts with the vapor given off by the filament.
3. The filament acts catalytically on the gas, producing a chemical change in the gas without any permanent change in the filament.
4. The gas is chemically changed, or is made to react with the filament by means of electrical discharges through the gas.

Direct Attack of the Filament.

1. Clean-up of Oxygen by a Tungsten Filament.²—The action of oxygen on a tungsten filament is one of the best examples of this type of reaction. In air at atmospheric pressure tungsten begins to oxidize at about 400–500° C. and becomes coated with an iridescent film much as steel does. At higher temperatures the oxidation becomes rapid and a scale of the yellow oxide WO_3 forms on the metal. At temperatures above 1500° K. the oxide volatilizes so rapidly that it forms a dense, white smoke. Under such conditions the rate of oxidation evidently depends on the rate at which the oxygen can diffuse up to the surface of the metal through the nitrogen and through the layer of oxide on the surface. Such a large number of factors is involved that it would seem very difficult to derive much information as to the mechanism of the chemical reaction from experiments at these high pressures.

The case is quite different, however, when we study the action of a heated tungsten filament on oxygen at a pressure as low as, say, 100 bars. We then find that at temperatures above about 1200° K. the tungsten is attacked, producing the yellow oxide WO_3 , but that this distills off as fast as it is formed, leaving the surface clean and bright.

The pressure of oxygen decreases in the manner shown in Fig. 1. The rate of clean-up is initially high, but gradually becomes smaller as the oxygen pressure becomes less. It is found that the slope of this curve at any point is proportional to the pressure at that point. In other words, the velocity of the reaction is proportional to the pressure. This is the law according to which a monomolecular reaction proceeds, and is also

¹ *Phys. Rev.*, 2, 450 (1913).

² *THIS JOURNAL*, 35, 105 (1913).

the law which Nernst found to hold for reactions in which the velocity was limited by the rate of diffusion.

By Equation 5 we can calculate the rate at which the oxygen at a given pressure comes into contact with the filament. We can then compare

this rate with the rate found experimentally for the same pressure. By dividing the two, we find what fraction of all the molecules that strike the filament react with it. Let us call this fraction ϵ . Of course this fraction must be less than unity, for the reaction cannot possibly take place more rapidly than the rate at which the molecules can come

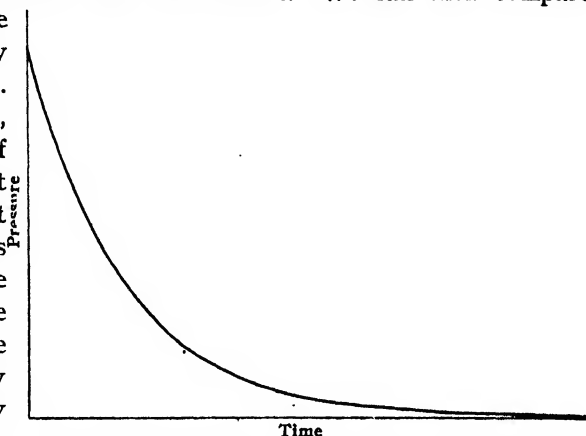


Fig. 1.—Typical curve for the clean-up of oxygen.

into contact with the surface. Experimentally, we have shown that the rate of clean-up is proportional to the pressure. Since the rate at which the molecules strike the filament is also proportional to the pressure by (5), it is evident that ϵ is the same at all pressures in the range covered by the experiments. Table I shows the values obtained for ϵ from experiments at different filament temperatures. We see that ϵ is always less than unity, as of course it must be, but at the highest temperatures it seems to be approaching a limit which is below unity. At the lowest temperatures ϵ has a very large temperature coefficient, much higher than if we were dealing with a reaction of the types studied by Nernst with a diffusion film of constant thickness.

TABLE I.—RATE OF CLEAN-UP OF OXYGEN.

| | | | | | | | | | |
|------------------|----------|--------|--------|--------|--------|-------|-------|------|------|
| Temp..... | 1070° K. | 1270 | 1470 | 1570 | 1770 | 2020 | 2290 | 2520 | 2770 |
| ϵ | 0.00033 | 0.0011 | 0.0053 | 0.0094 | 0.0255 | 0.049 | 0.095 | 0.12 | 0.15 |

Experiments were made with the bulb cooled by liquid air and also heated to 300° in an oven. The rate of reaction was found to be independent of the bulb temperature.

Let us now examine these experimental data and see what conclusions can be drawn as to the mechanism of the reaction.

Since the oxide formed is WO_3 , it is evident that at least two molecules of oxygen must react with each atom of tungsten.

There are two possibilities to consider. Either both the oxygen molecules simultaneously strike a single tungsten atom or else an oxygen

atom or molecule must already be present on the surface at the point where the second molecule strikes.

We have already seen that the number of oxygen molecules striking the surface per second within an area of molecular dimensions is $170 \times p$. The velocity of the molecule is 44,000 cm. per sec. If we consider a molecule which strikes the surface and rebounds, the length of time it remains within molecular dimensions of the surface is the time taken to travel twice the diameter of the molecule, or 5.4×10^{-8} cm. In other words, the duration of a collision is only 1.2×10^{-12} seconds. Since there are $170 \times p$ collisions per second, the total time in each second during which molecules are present at a given point is $170 \times 1.2 \times 10^{-12} p$ or $2.1 \times 10^{-10} p$. This gives us directly the probability that a molecule striking a given point on the surface will find a molecule of oxygen already present. Thus, if we had to depend on simultaneous collisions we see that ϵ could not exceed $2.1 \times 10^{-10} p$. This is vastly less than the values of ϵ actually observed. At a pressure of 10 bars this would give for ϵ a value of only 2×10^{-8} , whereas at the higher temperatures we have found values as high as 0.15. A further objection to the hypothesis of simultaneous collisions is that it would lead to values of ϵ which are not independent of the pressure. With this hypothesis, the reaction velocity would be proportional to the square of the pressure (bi-molecular reaction).

We must therefore conclude that the oxygen molecule striking the surface reacts with those already present. There is thus definite proof that some sort of film containing oxygen is present on the surface.

This film, however, cannot be in equilibrium with the space around it, as was assumed in Bodenstein and Fink's theory. Since the oxide formed travels directly to the bulb and condenses, there is no possibility that any appreciable number of molecules of oxide return to the filament.

On the other hand, it is not possible to assume that each molecule of oxygen striking the filament remains there a short but indefinite time before distilling off. In this way it would be possible to account for any given value of ϵ , but the velocity of the reaction would then be proportional to the square of the pressure rather than the first power.

From another point of view, we also must conclude that there is a film on the surface which determines the velocity of the reaction. We have seen that at the lower temperatures only a small fraction of the molecules which strike the filament react. According to the ordinary conception of a reaction in a homogeneous system, it is the relative velocity of two molecules with respect to each other at the moment of contact which largely determines whether or not they will react. The higher the relative velocity, the greater the chance of reaction is supposed to be. The experiments in the present case have shown that the rate of reaction does

not depend on the relative velocity of the molecules, since changing the temperature of the bulb had no effect. What is it, then, that determines whether a given oxygen molecule shall react or not? It must be something that depends solely on the condition of the surface of the filament.

We have just seen that the older theory, which supposes that it is the thickness of an adsorption film which determines the velocity, leads us into difficulties. Let us now look upon the problem from the point of view of the new theory, according to which the adsorption film is only one molecule thick.

Since the experiments have shown that ϵ is independent of the pressure, it is natural to assume that the condition of the surface responsible for determining the reaction velocity, is also independent of the pressure. This requirement would be met if we assume that the surface film covers the surface nearly completely and consists of two kinds of molecules in thermal equilibrium with each other. One of the kinds of molecules is to be regarded as capable of reacting directly with the oxygen striking the surface, while the other is incapable of so doing. The conclusion that the surface must be nearly completely covered with an adsorption film of oxide is based largely on experiments on the electron emission, where it is found that a pressure of oxygen even as low as 0.01 bar cuts the electron emission from tungsten at 1900° K., down to less than 1% of its value in the absence of oxygen.

In formulating the above theory more precisely we may proceed as follows:

Let us assume that of all the oxygen molecules striking the bare surface of tungsten, the fraction α is absorbed or sticks to the surface, the fraction $1 - \alpha$ being reflected or rebounding from the surface. Only a very small fraction of the surface, however, is bare and we may assume that the oxygen molecules striking a surface already covered, are not absorbed in this way. If we let θ represent the fraction which is bare, then of all the oxygen molecules striking the whole surface only the fraction $\alpha\theta$ is absorbed. Now the rate at which the oxygen molecules strike the surface is given by Equation 5 and we see that it is proportional to the pressure. We thus see that the rate at which oxygen is absorbed by the surface is

$$\alpha \theta p$$

if we neglect for convenience the constant factor in Equation 5.

To form a more concrete picture of the mechanism of the reaction, let us assume that the oxygen on the surface is at first in the form of the compound WO_2 , but that this reacts with the tungsten in contact with it to form $2WO$, and that this reaction is reversible and that equi-

librium prevails between the two compounds.¹ According to the law of mass action, the surfaces covered by the two compounds will have to fulfill the relation

$$\theta_1 = K\theta_2$$

where K is the equilibrium constant and θ_1 is the fraction of the surface covered by WO_2 and θ_2 is the surface covered by WO .

It is now natural to assume that if oxygen striking the surface collides with a WO_2 molecule, no reaction takes place, but that when the oxygen strikes a WO molecule it reacts to form WO_3 , which distills off. Of all the O_2 molecules striking the WO we may, for the sake of generality, assume that only the fraction ϵ_2 reacts.

From these considerations it is easy to state the problem mathematically as follows:

$$\alpha \theta p = \frac{1}{2} \theta_2 \epsilon_2 p \quad (7)$$

$$\theta_1 = K\theta_2 \quad (8)$$

$$\theta + \theta_1 + \theta_2 = 1 \quad (9)$$

The first equation states simply that the rate at which the oxygen is adsorbed is equal to the rate at which it is removed by the reaction. The coefficient $\frac{1}{2}$ is necessary because each molecule of oxygen striking the filament only removes one atom ($\frac{1}{2}$ molecule) of oxygen from it in forming WO_3 . The second equation merely expresses that equilibrium exists between the WO_2 and the 2 WO , and the third equation states that the bare surface is equal to that which is not covered by the WO_2 and the WO . For a more general solution of the problem we may also take into account the fact that the WO_2 and the WO are probably evaporating or dissociating to some extent and that the WO_3 that is formed requires some time before it evaporates. The equations obtained in this way are more complicated than those above, but can easily be worked out. The results in the present case are not essentially different from those we obtain by the above equations.

From the three equations above we may eliminate θ , θ_1 and thus obtain

$$\theta_2 = \frac{2\alpha}{\epsilon_2 + 2\alpha(K + 1)} \quad (10)$$

The rate R at which the oxygen is converted into WO_3 is

$$\frac{3}{2} \epsilon_2 \theta_2 p$$

or

¹ This assumption of the existence of the compounds WO and WO_2 on the surface is made only to form a picture of a possible mechanism. It is much more probable that the oxygen atoms are chemically combined with tungsten atoms which form the surface of the filament and which are part of the "space lattice", of the tungsten crystals.

$$R = \frac{3\alpha\epsilon_2 p}{\epsilon_2 + 2\alpha(K + 1)} \quad (11)$$

This shows that the rate of clean-up by this theory is proportional to the pressure, in agreement with the experiments. If every oxygen molecule which struck the filament reacted, the rate of clean-up would be p (neglecting the same constant factor as before) and hence the value of ϵ which we determined from the experiments and have given in Table I, would be

$$\epsilon = \frac{3\alpha\epsilon_2}{\epsilon_2 + 2\alpha(K + 1)} \quad (12)$$

This is independent of the pressure. It is probable that ϵ_2 and α are nearly independent of the temperature and that the large temperature coefficient of ϵ is due to that of K . Thus, at low temperatures, K must be very large, which means that the amount of WO in equilibrium with the WO_2 is very small. As the temperature rises, K decreases and ϵ therefore increases, but finally reaches a limiting value,

$$\epsilon_{\max.} = \frac{3\alpha\epsilon_2}{\epsilon_2 + 2\alpha} \quad (13)$$

which is always less than unity. This is in splendid agreement with the experiments. In order that $\epsilon_{\max.}$ may be as large as 0.2, the value estimated from Table I, it is necessary that ϵ_2 shall be greater than 0.2 and that α shall be greater than 0.1. That is, at least 0.2 of the O_2 molecules, colliding with WO molecules must react and at least 0.1 of the oxygen molecules striking the bare surfaces must be absorbed or react to form WO_2 .

By this theory it may be predicted that with still higher filament temperatures ϵ will begin to decrease when a point is reached at which the WO_2 and WO evaporate or dissociate so rapidly that only a small fraction of the surface is covered. For similar reasons it may be predicted that ϵ cannot remain independent of the pressure down to the lowest pressures. There is excellent experimental evidence that the last prediction is in accord with the facts. It is found that an extremely low pressure, probably less than 0.001 bar, of oxygen in a tungsten lamp not only does not perceptibly attack the filament, but actually prevents the tungsten which evaporates from discoloring the bulb. This action is probably due to the dissociation of the WO on the filament producing atomic oxygen which, traveling to the bulb, reacts with the deposited tungsten even at room temperature, to form WO_3 . In a later paper I hope to take up this point in more detail and consider the phenomena quantitatively from the view-point of the theory I have outlined this evening.

I have spent much more time on this reaction between tungsten and

oxygen than its experimental importance warrants, but I wished to illustrate by it in some detail the application of the theory of molecular films.

2. Reactions between Chlorine and Tungsten.—Chlorine at low pressures attacks tungsten, forming WCl_6 . The velocity of the reaction reaches a maximum at about $1500^\circ K.$ and becomes extremely small at higher temperatures. This is undoubtedly to be explained by the dissociation of some of the intermediate products which are necessary steps in the formation of WCl_6 . The chlorine leaving the filament is largely dissociated into atoms under these conditions and produces some extremely interesting effects which I shall discuss more in detail a little later.

3. Reactions between Carbon and Oxygen.—It has long been a disputed question whether carbon monoxide is a direct product of the oxidation of carbon or whether it is formed only by the interaction of carbon with carbon dioxide produced as a primary product.

By heating a carbon filament in oxygen at very low pressures in a bulb immersed in liquid air, a definite answer to this question is readily obtained. If carbon dioxide is produced and leaves the filament, it must travel directly to the bulb and there be condensed at the low temperature of liquid air where the vapor pressure of carbon dioxide is barely measurable. The filament therefore never comes in contact with carbon dioxide.

The first experiments showed that the phenomena involved in the oxidation of carbon are very complex as compared with those of the oxidation of tungsten. With tungsten the results were always accurately reproducible, but with the carbon filaments the rate of clean-up depended entirely upon the previous history of the filament.

In the experiments metalized carbon filaments were used. These consist of a highly graphitized carbon of the highest attainable purity (ash about 0.01%). After mounting in the lamp the filament was heated in a high vacuum for several hours until it ceased giving off measurable quantities of gas. Small quantities of oxygen at a pressure about 5–10 bars, were admitted and the rate of clean-up with different filament temperatures was noted.

With the filament at $1220^\circ K.$ the oxygen began to disappear very rapidly, but soon slowed down to a rather uniform slow rate. At this temperature the whole of the oxygen gradually disappeared and CO_2 , without a trace of CO , was formed. The amount of CO_2 , however, was considerably less than the equivalent of the oxygen which disappeared. On adding a second supply of oxygen the rate of clean-up was very much slower than the first time. After three or four treatments the rate of clean-up finally became reproducible. On raising the filament temperature to $1700^\circ K.$ the rate of clean-up increased again, but gradually

decreased as before. In the first treatment, at 1700°K. , all the oxygen disappeared and no CO was formed, but in subsequent treatments at the same temperature there began to be formed increasing amounts of CO. After five or six runs in oxygen, pumping out the residues of CO each time, the pressure would decrease only 10 or 20% when the filament was lighted in a fresh supply of oxygen, and would then increase until finally a residue of pure CO would remain, having a volume usually about 30% greater than that of the oxygen used.

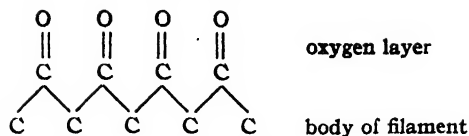
If the filament was now heated in vacuum, it gave up CO extremely slowly at 1700°K. , but at 2200°K. the evolution was much more rapid, although even at this temperature from half an hour to an hour was required before the evolution ceased. The total amount of CO so obtained usually amounted to 3-5 cu. mm. After having thus heated the filament in vacuum, the first run in oxygen with the filament at 1700°K. gave nothing but carbon dioxide, but the runs following this gave, as before, an increasing amount of carbon monoxide.

With the filament at 2100°K. in oxygen, there was always a large quantity of carbon monoxide produced, even in the first run.

These experiments seem to show that when oxygen acts on carbon at, say, 1200°K. , part of the oxygen reacts to form CO_2 , but another part forms an adsorption layer of some sort on the surface which retards the velocity of the reaction. This adsorption layer is probably chemically combined with the carbon, presumably as an extremely stable solid oxide of carbon.

At higher temperatures the rate of formation of this adsorption layer increases rapidly. When a sufficient quantity has accumulated this compound begins to decompose, forming carbon monoxide, the higher the temperature the more rapid being the formation of this gas.

Judging from the great stability of this adsorption layer, which enables it to be heated for half an hour at 2200°K. in the highest vacuum without being completely decomposed, a plausible guess as to its constitution is that it consists of oxygen atoms chemically combined with the carbon atoms which form the surface of the filament. According to our recent knowledge of the structure of solid bodies, we have the best of reasons for believing that the atoms of solid bodies are held together directly by chemical forces and that a crystal must be looked upon as a single molecule. The carbon atoms in the filament must thus be considered as forming endless carbon chains with each other. It is probably due to the great stability of these carbon chains that carbon has such a low vapor pressure and such a high melting point. In the present case, if we consider the oxygen atom to be chemically combined with one of the outer carbon atoms, we have a structure that could be represented by the formula



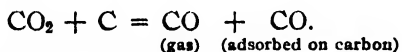
This hypothesis would seem to afford an unforced explanation of the extraordinary difficulty of removing oxygen and hydrogen from carbon.

Experiments were also made to study the action of the heated carbon filament on carbon dioxide and monoxide.

With carbon dioxide at 1220° K. no change occurred, but at 1700° K. carbon monoxide was formed at first slowly, and then gradually more rapidly. The total volume, however, usually remained nearly constant, showing that the reaction was not



but was rather



On the other hand, at temperatures up to 2400°, there was never any perceptible change in volume when the filament was heated in carbon monoxide, showing that the adsorbed compound is not formed by adsorption of carbon monoxide.

These results should be looked upon merely as preliminary results, and I hope to be able to present further details of the experiments with carbon and oxygen at a later date.

II. Reactions with Vapor from Filament.

Clean-up of Nitrogen by a Tungsten Filament.¹—When a tungsten filament is heated to 2700 or 2800° K. in nitrogen at low pressure, the nitrogen slowly disappears at a rate which is independent of the pressure.

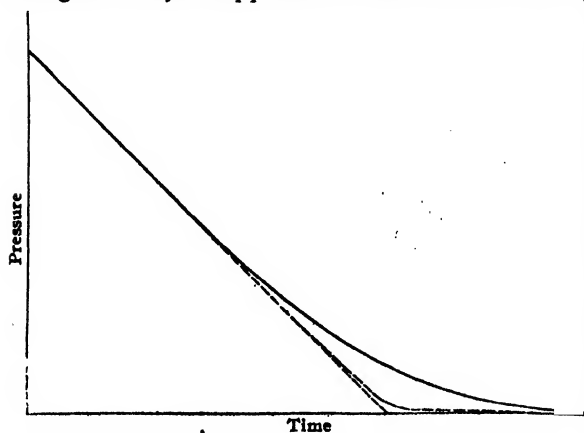


Fig. 2.—Typical curve for the clean-up of nitrogen.

Fig. 2 gives a good example of the way the pressure decreases in a typical experiment. At the high temperatures employed in these experiments it has been found that the filament evaporates fairly rapidly. A comparison of the amount of nitrogen cleaned up with the loss of weight of the filament, showed that the ratio was the same as

¹ THIS JOURNAL, 35, 931 (1913).

that in a compound of the formula WN_2 . This ratio still held if the temperature of the filament was raised several hundred degrees, where the rate of clean-up was over four hundred times more rapid. Measurements showed that the rate of loss in weight of the filament in low pressure nitrogen was the same as in vacuum, so it was evident that the nitrogen did not attack the filament.

In these experiments the tungsten does not collect on the bulb as the usual black deposit, but was of a clear, brown color. On opening the bulb and admitting moist air the brown color disappeared and a strong smell of ammonia was observed.

It is evident that the nitrogen in this case combined with the tungsten vapor as fast as it is given off. By working at such low pressures that only a few of the tungsten atoms collided with nitrogen molecules on the way to the bulb it was proved that practically every collision between the nitrogen molecules and tungsten atoms resulted in the formation of the compound. In other words, the coefficient ϵ is unity. We are here dealing then in reality with a bimolecular homogeneous reaction of maximum possible velocity.

The true reaction velocity is independent of the temperature. What is measured in the experiment is only the rate at which the tungsten evaporates.

Recent experiments have shown that the rate of clean-up of the nitrogen at higher pressures is the same whether the bulb is heated to 300°C . or is cooled in liquid air. But at lower pressures an interesting difference occurs, which is shown by the dotted curve in Fig. 2. With the bulb at room temperature the curve departs from the straight line at the lower pressures because the nitrogen molecules become so scarce that a large fraction of the tungsten atoms strike the bulb without colliding with nitrogen molecules. From the agreement between the calculated and observed curves at the lowest pressures, it was reasoned (in the paper on the nitrogen clean-up) that the tungsten atoms striking the glass deposit as such, do not combine with nitrogen. This suggested that few, if any, nitrogen molecules are present on the glass at room temperature. The more recent experiments now prove that when the bulb is cooled in liquid air the tungsten atoms do combine with nitrogen even if the pressure is so low that they do not strike them on the way to the bulb. The shape of these curves at low pressures proves that the glass surface, or rather that of the tungsten nitride layer on the glass, at liquid air temperature is covered by an adsorbed film of nitrogen, but at room temperature it is not. This method can even be used to calculate quantitatively the fraction of the surface that is covered by the nitrogen at any given temperature.

Clean-up of Nitrogen by a Molybdenum Filament.—Molybdenum evaporates much more readily than tungsten, and it was thought that

nitrogen would therefore be cleaned up more easily by a molybdenum than by a tungsten filament. This was not found to be the case. On further investigation it was found that the molybdenum lost weight at the same rate as in vacuum and that the rate of clean-up was independent of the pressure, as in the case of tungsten, but that the amount of gas cleaned up was only about one-tenth of that which would have been observed if every molybdenum atom combined with a nitrogen molecule.

Under these conditions we should expect that the rate of clean-up would vary with the pressure, for the higher the pressure the more collisions the molybdenum atoms must make with the nitrogen molecules before striking the bulb. In order to account for the fact that the rate of clean-up is independent of the pressure, it is necessary to assume that if combination does not take place during the first collision it does not take place at all. The question arises: What is the difference between the first and the subsequent collisions which can account for the different behavior in the two cases? Since the nitrogen molecules are the same in both cases, the difference must lie in the molybdenum atoms. Now, according to our ordinary conceptions, atoms can differ from each other only in respect to their translational velocity.¹ Since the velocities of the molybdenum atoms leaving the filament are higher than those after collision with nitrogen molecules, it would seem that this could readily explain the fact that combination can occur only on the first collision.

If this were the case, then raising the temperature of the filament should increase ϵ ; that is, the percentage of successful collisions. Actually, however, the reverse was found. By lowering the filament temperature 100° , ϵ increased from 0.11 to 0.33, and by raising it 100° , ϵ decreased to 0.05. The effects of varying the bulb temperature were still more striking. With the bulb in liquid air, ϵ became about 0.4 and by heating the bulb to 270° C. ϵ became 0.01.

In other words, the reaction velocity has a very marked negative temperature coefficient; there is thus a much larger fraction of successful collisions if the relative velocities of the nitrogen molecules and molybdenum atoms are small at the moment of collision.

This, however, makes it still more difficult to explain why the reaction can occur only at the first collision, for it would seem that if the first collision were unsuccessful the subsequent collisions would be more likely to result in combination because the velocities would then be lower.

I think the solution of this difficulty is to assume that the first collision always results in a union of the nitrogen and molybdenum so that they travel together to the bulb, but that this union may occur in one of two ways, depending upon the relative velocity of the molecule and atom at

¹ Experiments show that neither the nitrogen nor the molybdenum is electrically charged.

the moment of their collision. If the relative velocity is high, the union is so weak that the two components fall apart when the unstable molecule strikes the bulb. On the other hand, if the relative velocity at the moment of contact is small enough, actual chemical combination occurs.

This may seem a rather far-fetched theory, but there is a very large amount of experimental evidence in its favor which I have not time to go into this evening. A paper describing these results in more detail is now nearly ready for publication.

The striking fact that the velocity of the actual chemical reaction has a large negative temperature coefficient will be considered again in connection with other experiments. It must be pointed out, however, that this effect is only noticed because of our analysis of the reaction into its separate partial reactions. If the temperature of the gas and filament varied together and if the function of the molybdenum vapor were not known, the effect would never be noticed, for the large positive temperature coefficient of the rate of evaporation of molybdenum would completely mask that of the true chemical reaction.

In these experiments the molybdenum deposit which collected on the bulb had very remarkable properties. It adsorbed large quantities of nitrogen, but not hydrogen, if cooled by liquid air. But, at room temperature and above, it could slowly dissolve large quantities of hydrogen which it would slowly give up again at 300° C. Although it contained a large amount of nitrogen, none of this gas could be driven off by heating it at 360°; but if it was heated in nitrogen at 250° C. it apparently combined with the nitrogen, for this gas was absorbed and was not liberated by heating at 360° C. in a vacuum.

Another characteristic of this deposit was that it reacted rapidly at room temperature with water vapor, producing hydrogen, most of which remained dissolved and was liberated on heating.

Molybdenum deposited on the bulb in high vacuum does not exhibit any of these characteristics. It seems that the molybdenum described above, is in an atomic state of division as a result of being deposited atom by atom by the decomposition of the unstable compound formed in the "unsuccessful collisions."

Clean-up of Carbon Monoxide by Tungsten.—With the bulb at room temperature this gas behaved exactly like nitrogen. In fact, with the filament at a given temperature, the curves obtained first with nitrogen and then with carbon monoxide proved to be identical. This proved that each atom of tungsten combined with one molecule of CO, presumably to form a compound WCO. The coefficient ϵ must have been unity as in the case of nitrogen.

Since with nitrogen and molybdenum ϵ was found to vary with the tem-

perature, it was of interest to see if ϵ with carbon monoxide and tungsten might not vary also.

Raising the bulb temperature to 300° gave a value of ϵ distinctly less than at room temperature, so that the expected effect was present and in the same direction as with the Mo-N₂ reaction.

When a similar experiment was tried with the bulb in liquid air, the surprising result was obtained that on lighting the filament the gas cleaned up about five times as fast as with the bulb at room temperature. Further experiments showed that the filament under these conditions lost weight about five times as fast as in a vacuum, so that the filament was clearly being attacked by the carbon monoxide. The rate of clean-up, however, was still linear; in other words, was independent of the pressure. Evidently, the compound formed was of approximately the same composition as that formed by interaction with the vapor, namely WCO.

There is apparently no escape from the conclusion that the attack of the filament by CO is a reaction which takes place more rapidly when the velocity (or at least kinetic energy) of the CO molecules is small. We thus again have a case of negative temperature coefficient.

The simplest explanation of the fact that the rate of attack is independent of the pressure, seems to be that the velocity of the reaction is so great that the rate of evaporation of the compound formed determines the rate of reaction.

Thus we assume that the surface is practically completely covered with a film (1 molecule deep) of WCO. As fast as molecules of this distil off, the surface of tungsten is exposed to the attack of the CO.

If this explanation is correct, then as long as the bulb temperature is low enough to cause the formation of a film of WCO, it is evident that a further lowering of the bulb temperature should cause no further increase in rate. Another conclusion may be drawn. At a bulb temperature so high that the supply of WCO is barely sufficient to keep the surface covered, we should expect that the rate of clean-up at the lower pressures would be less than at higher. In other words, there should be certain intermediate temperatures at which the rate of clean-up is no longer linear.

The experiments made to test these points have yielded results in quantitative agreement with the theory. Thus it was found that the rate of clean-up at -78° C. (solid CO₂) was the same as at -190° C., and on the other hand the rate at -20° was the same as at $+20^{\circ}$. But at -40° the rate was intermediate between that at -78° and that at -20° , and, furthermore, the curve was no longer straight, but was in splendid agreement with a calculated curve which was based on the assumption that the rate of formation of WCO on the *exposed surface* of tungsten was proportional to the pressure of CO.

I think this case is an excellent illustration of the general applicability

of what I might call the molecular film theory of heterogeneous reactions.

In this case also I hope soon to publish quantitative data with a more completely developed theory.

Clean-up of Oxygen by Platinum.—A platinum filament at temperatures above about 1600° K. gradually causes the clean-up of low pressures of oxygen. With pressures less than 100 or 200 bars the rate is independent of the pressure. The filament loses weight at the same rate as in vacuum. Quantitative measurements show that the oxygen combines with the platinum atoms as fast as they evaporate from the filament and form the compound PtO_2 which collects on the bulb as a brown deposit. At higher pressures the oxygen also begins to attack the platinum at a rate dependent on the pressure.

III. Catalytic Reactions.

Dissociation of Hydrogen into Atoms.¹—It has been shown that when a wire of tungsten, platinum, or palladium is heated to a temperature above 1300° K., in hydrogen at very low pressure (1–20 bars), a portion of the hydrogen molecules which strike the filament is dissociated into atoms. This atomic hydrogen has remarkable properties. It is readily adsorbed by glass surfaces at room temperature, although more strongly at liquid air temperatures; but only a very small amount (a few cu. mm.) can be so retained because the atoms evidently react together to form molecular hydrogen as soon as they come in contact, even at liquid air temperatures. The atomic hydrogen reacts instantly at room temperature with oxygen, phosphorus and many reducible substances such as WO_3 , PtO_2 , etc.

When a tungsten wire is heated to very high temperatures (above 2000°) in hydrogen, the dissociation of the gas in contact with the wire causes the absorption of a very large quantity of heat. The atomic hydrogen produced diffuses out from the wire and as soon as it reaches a cooler region recombines to form molecules and liberates the heat of the reaction. The result is that the heat conductivity of hydrogen, at temperatures where dissociation occurs, is several times larger than it would otherwise be.

Recently, Mr. Mackay and I have made a series of measurements on the heat losses from tungsten wires at pressures ranging all the way from 10 bars up to atmospheric pressure and at temperatures up to the melting point of tungsten. From these data I have been able to show that the dissociation of the hydrogen does not occur in the space around the wire, but takes place only among the hydrogen molecules which have been absorbed or dissolved by the metal. The mechanism is as follows:

¹ *Trans. Am. Electrochem. Soc.*, 20, 225 (1911); *THIS JOURNAL*, 34, 860 (1912); 34, 1310 (1912); 35, 927 (1913); 36, 1708 (1914); 37, 417, (1915); *Z. Elektrochem.*, 20, 498 (1914).

All the hydrogen atoms striking the surface of the wire and about 70% of all the molecules striking the wire are absorbed by it. The velocity of the reaction between the molecules and atoms of hydrogen absorbed is so great that equilibrium prevails among them at all times. The rate of dissociation of the hydrogen by the wire can thus be calculated from the dissociation constant of the hydrogen and from Equation 5, which gives us the rate at which the gas comes into contact with the wire. By reversing this process it has been possible to determine the degree of dissociation of hydrogen at all temperatures and pressures and to calculate the heat of dissociation. At 2000°K. , hydrogen is 0.33% and at 3000°K. , 13% dissociated at atmospheric pressure.

Dissociation of Chlorine into Atoms.—By heating a tungsten filament for a short time to 3000°K. in a high vacuum a sufficient quantity volatilizes to form a black deposit on the bulb. If, now, a low pressure of chlorine be admitted to the bulb, this does not perceptibly attack the deposit on the bulb nor the filament, even if the bulb is heated to 200°C. However, if the filament is now heated to a high temperature, while the bulb is kept cool, the tungsten deposit on the bulb soon disappears. The chlorine has evidently been activated or dissociated by the filament and the atoms formed travel at these low pressures directly from the filament to the bulb without having any chance to recombine on the way.

The experiment is more striking if two filaments be placed side by side in the same bulb containing a very low pressure of chlorine. If one of the filaments be heated to a high temperature it is found that the other one, which remains cold, is gradually eaten away on the side facing the hot filament until it finally disappears completely. The hot one does not lose at all in weight, but may even become heavier, by having tungsten deposited on it by the decomposition of the chloride formed by the attack of the cold filament.

Dissociation of Oxygen into Atoms.—In connection with the clean-up of oxygen by a tungsten filament I have already spoken of some of the evidence for the dissociation of oxygen into atoms at extremely low pressures. Still better evidence has been obtained in some experiments on thermionic currents in which the bulb containing the filaments is immersed in liquid air. Under these conditions an active form of oxygen can be collected on the glass which is slowly given off and reacts even at liquid air temperatures with tungsten. The phenomena are in many ways similar to those observed with hydrogen. A further quantitative study of the formation of this active oxygen is being undertaken.

Reaction between Carbon Monoxide and Oxygen in Contact with Platinum.—In all the reactions I have spoken of, thus far, there has been only one gas in contact with the filament. The case where the filament is brought into contact with two gases is an important one and

warranted special study. For this purpose a short filament of fine platinum wire was mounted in the center of a four-liter bulb. Pressures of carbon monoxide and oxygen up to a total of about 30 bars were admitted and the filament was heated to such a temperature that the reaction proceeded at a convenient rate. A large tube extended from the lower part of the bulb and was kept immersed in liquid air, so that the molecules of carbon dioxide produced in the reaction were condensed before they had any opportunity of striking the filament.

The results were very striking. The rate of clean-up was found to be directly proportional to the pressure of oxygen, but *inversely proportional* to the pressure of carbon monoxide. Reference to the literature showed that Bodenstein and Ohlmer,¹ in their study of the reaction between these gases on quartz glass surfaces, had found these same relations at about atmospheric pressure. Subsequently, Bodenstein and Fink² suggested tentatively that the explanation of this peculiar behavior might be that the surface of the quartz is covered with an adsorbed film of carbon monoxide of a thickness proportional to the pressure of this gas. If it was further assumed that the oxygen had to diffuse through the layer of carbon monoxide and come into contact with the platinum before it could react with the monoxide, then the reason for the reaction being directly proportional to the oxygen pressure and inversely proportional to that of the carbon monoxide was apparent.

There were serious objections to applying this theory in the present case, for in order that the thickness of a film could be proportional to the pressure over a wide range of pressures it would be necessary to have a film many molecules deep, and this seemed very improbable at the low pressures used in these experiments.

If, on the other hand, we apply the "theory of molecular layers," these difficulties disappear. Let us assume that, of all the CO molecules striking the surface, a certain fraction α , are condensed and that the CO layer thus formed distills off at a certain rate. Let us assume further that the reaction occurs when CO molecules strike oxygen on the surface, but does not occur when O₂ molecules strike CO molecules. We might picture the cause of this as being due to the carbon monoxide molecules on the surface arranging themselves with the carbon atoms in contact with the platinum, while the oxygen atoms cover these and thus protect the carbon from attack by the oxygen.

It is easy to state these assumptions mathematically and thus derive an equation giving the rate of the reaction in terms of the partial pressures of the gases. This relation is of the form:

¹ *Z. physik. Chem.*, 53, 166 (1905).

² *Ibid.*, 60, 46 (1907).

$$R = \frac{I}{\frac{ap_1}{p_1} + \frac{b}{p_1} + \frac{c}{p_2} + \frac{d}{p_1 p_2}} \quad (14)$$

where p_1 is the partial pressure of CO and p_2 is that of the oxygen. The coefficients a , b , c and d all have a definite physical significance in this theory, but I will not go into this at present.

It is readily seen that at higher pressures the terms involving b , c and d become negligible compared to that involving a . The p_2 in this term goes into the numerator and we have

$$R = p_2/ap_1. \quad (15)$$

which is the law observed in the experiments I have described.

On the other hand, at lower pressures or at higher temperatures, the first term in the denominator becomes negligible and the fourth term still remains so and the relation becomes

$$R = \frac{I}{\frac{b}{p_1} + \frac{c}{p_2}} \quad (16)$$

At still lower pressures or higher temperatures the last term in the denominator would become the important one and the equation would reduce to

$$R = p_1 p_2/d. \quad (17)$$

This theory thus suggested that if higher filament temperatures were used in the experiments the rate would no longer be in accord with Equation 15 but would follow Equation 16. Furthermore, the term containing d involved the rate of evaporation of the CO and O₂ from the surface in such a way that it must increase with the temperature. The velocity of the reaction would therefore decrease at higher filament temperatures.

To test this prediction it was necessary to use a filament of extremely short length (1 cm.) and very small diameter (0.003 cm.), so that the rate of clean-up would not be too rapid to measure. Under these conditions it was found that the rate of clean-up actually reached a maximum at a temperature below a red heat, and at a bright red heat the rate was only about one-tenth of that at the lower temperature.

By studying these data in the light of this theory, I am confident that it will be possible to calculate in detail the statistics of this reaction; for example, the rate of evaporation of each constituent, the proportion of the collisions between the CO and the oxygen which result in combination, etc.

Reaction between Hydrogen and Oxygen in Contact with Platinum.—This reaction proves at low pressures in absence of water vapor to be essentially similar to that between carbon monoxide and oxygen. At low

temperatures the rate of reaction is directly proportional to the pressure of oxygen and *inversely proportional to that of the hydrogen*. At higher temperatures the rate varies with the pressure as indicated by Equation 16, but in contrast to the behavior of oxygen and carbon monoxide, the velocity does not decrease when the temperature is raised even to the melting point of the filament.

Other Catalytic Reactions.—The theory here outlined would seem to be generally applicable to all heterogeneous reactions, even at atmospheric pressure. The many reactions studied by Bodenstein lend themselves admirably to testing out this theory.

There is every indication that the experimental results of Fink will be in at least as good agreement with equations derived by this theory as with those derived from the theory that involves diffusion through a film of variable thickness. For a given concentration of SO_2 the equations take the form

$$R = \frac{1}{\frac{b}{p_1} + \frac{c}{p_2}}. \quad (18)$$

When one constituent is in excess the reaction velocity is thus proportional to the concentration of the other. When there are equivalent proportions, then the velocity is proportional to the total pressure. These are the relations found by Fink, but here one equation fits all the results, whereas by Fink's theory two equations are necessary.

Theory of Adsorption.—The "theory of molecular layers" leads to a simple but quantitative theory of adsorption.

In every reaction we have studied we have found that of all the molecules striking a surface, a large proportion are absorbed. If the rate of evaporation is high the molecules will leave the surface very soon, while if the rate of evaporation is low they may remain a long time. The adsorption is due to the fact that a certain time must elapse between the condensation and the evaporation of a molecule.

In the case of strongly adsorbed bodies, or in all cases where the vapor is nearly saturated, we must take into account the condensation and evaporation in the second and subsequent layers. If we assume that the rate of evaporation in the first layer is different from that for the others, this theory, stated mathematically, leads to an equation of the form

$$Q = \frac{1}{\frac{a}{p} + b - cp} \quad (19)$$

where Q is the amount adsorbed at the pressure p .

This theory will be developed in detail in a subsequent paper.

IV. Reactions Caused by Electrical Discharges.

If a positive potential of a hundred volts or so is applied to an auxiliary electrode in a bulb containing a heated filament, electrons are given off from the heated filament and these, in passing through the gas, may produce ionization. The positive ions then are attracted to the hot filament and strike it with high velocity. Under these conditions reactions often occur which otherwise would not take place. For example, if the gas is nitrogen, these positive ions will combine with the tungsten filament to form the nitride WN_2 even at temperatures where there is normally no appreciable volatilization of the tungsten.

Similar effects are observed with hydrogen and carbon monoxide.

The effects are in general more complicated than those observed in the purely thermal reactions, and largely for that reason I shall not consider them further at present. The phenomena, however, are of very great interest and will probably be the subject of many further investigations.

General Considerations.

This evening I have attempted to present to you a rather new view-point by which we may regard heterogeneous chemical reactions. By working at very low pressures it has been possible to learn much about the mechanism of these reactions.

In each case we have seen that the velocity of the reaction has been limited by the rate at which the reacting molecules come into contact with each other.

With reactions occurring on the surface of the wire, only a small fraction of the surface was in condition suitable for the reaction. The rate of reaction in these cases was limited by the rate at which the gas molecules could strike that part of the surface where the reaction could occur. In no case was there any evidence that the reaction was limited by any diffusion process in the ordinary sense.

In the case of reactions where the gas combined with vapor from the filament, the rate was again limited by the rate at which the molecules came in contact. All those that made contact reacted.

Only in two cases was it possible to measure a velocity which was not limited by such purely physical factors. These cases were the combination of nitrogen with molybdenum vapor and the attack of tungsten filament by carbon monoxide with low bulb temperatures. It is remarkable that in both these cases the temperature coefficient of the reaction velocity was strongly negative. In all the other reactions the large positive temperature coefficient was due to the fact that the rate of evaporation of the filaments or of adsorbed materials on them increases so rapidly with temperature.

I do not mean to imply that all the truly chemical reactions must have negative temperature coefficients, but the results strongly suggest that

such chemical reactions are very common, and that their effects are masked by other physical factors having large positive temperature coefficients.

The number of chemical reactions previously known which have negative temperature coefficients is extremely small. Bodenstein cites one case, that of the reaction: $2\text{NO} + \text{O}_2 = 2\text{NO}_2$.

Strutt found that atomic nitrogen recombines to form molecules much more rapidly at low temperatures than at high, and he reasons that a high translational velocity of the molecule should in general hinder rather than hasten the reaction. He considers that rotational velocity of the molecules, on the other hand, favors the reaction and that this factor in the majority of reactions greatly outweighs that of the translational velocity. Thus reactions between atoms should always have negative temperature coefficients, since atoms cannot have rotational energy. The present work lends further support to Strutt's views.

The view-point developed as a result of this work with low pressure reactions is undoubtedly applicable to reactions at high pressures and also to reactions between solids and liquids. It is hoped that further work will lead in a similar way to a better understanding of the mechanism of homogeneous reactions.

In conclusion, the writer wishes to express his appreciation of the valuable assistance of Mr. S. P. Sweetser, who has carried out most of the experimental part of this work.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE STATE UNIVERSITY OF KENTUCKY.]

CUPROUS SALTS OF OXYGEN ACIDS AND A NEW METHOD FOR PREPARING CUPROUS SALTS.

[PRELIMINARY PAPER.]

By LLOYD C. DANIELS.

Received March 19, 1915.

The number of cuprous salts of oxygen acids is so small, and those that are known are so unfamiliar, that it is not surprising that the misstatement is often made in text-books, even in the larger number of the more modern ones, that such compounds do not exist.

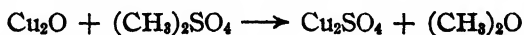
The longest known and most familiar member of this class of compounds is red cuprous sulfite, $\text{Cu}_2\text{SO}_3 \cdot \text{H}_2\text{O}$, first prepared by Rojoski.¹ Bourson² gives, as the best method for its preparation, the addition of a concentrated solution of sodium bisulfite to a solution of cupric sulfate, filtration from the slight precipitate, and gentle warming of the filtrate. Sulfur

¹ *Jahresber.*, 1851, 366.

² *J. prakt. Chem.*, 25, 399 (1842).

dioxide is evolved and the red compound crystallizes out. Rammelsberg¹ believed this compound to be a cuprous-cupric sulfite, $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$, but Etard² declares that the original conception of it is correct. It is also known in the form of a white isomer (Etard³).

Berzelius⁴ recognized the existence of cuprous sulfate in solution as probable from the fact that cooling a mixture, made by passing sulfur dioxide into hot cupric sulfate solution, produces a slight precipitate of metallic copper on cooling. This precipitate he attributed to a decomposition in the sense of the equation: $\text{Cu}_2\text{SO}_4 \rightarrow \text{Cu} + \text{CuSO}_4$. Two derivatives of cuprous sulfate were made before the mother-substance, itself, was isolated. Joannis⁵ prepared a carbon monoxide addition product, $\text{Cu}_2\text{SO}_4 \cdot (\text{CO})_4 \cdot \text{H}_2\text{O}$, by reduction of copper sulfate with copper in the presence of carbon monoxide. An ammoniated compound was prepared by Pechard⁶ by reduction of cupric sulfate in ammoniacal solution with hydroxylamine sulfate and precipitating with alcohol, by Bouzat⁷ by the action of ammonium sulfate on cuprous oxide in ammoniacal solution, and by Foerster and Blankenberg⁸ by electrolysis of an ammoniacal solution of cupric sulfate. It is a white crystalline compound of the formula $\text{Cu}_2\text{SO}_4 \cdot 5\text{NH}_3$. The free cuprous sulfate cannot be obtained by driving out the gaseous constituents of either of these derivatives; but it has been made by Recoura⁹ by the action of cuprous oxide on methyl sulfate:



It is described as a grayish white powder, stable in dry air and to heat (at least up to a temperature of 188° , since it was made by boiling with an excess of methyl sulfate), but it is quickly decomposed by moisture and in the sense supposed by Berzelius:



Acid cuprous thiosulfate, shining, golden needles, prepared by adding a solution of cupric sulfate to a solution of somewhat more than two mols of sodium thiosulfate, falls partly within this class. Its formula is $\text{Cu}_2\text{H}_4(\text{S}_2\text{O}_3)_3$. Cuprous metaphosphate in solid solution in excess of metaphosphoric acid was prepared by Auger.¹⁰ Cuprous acetate is briefly mentioned by Pechard³ as a white crystalline compound, $\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_2$,

¹ *Pogg. Ann.*, 67, 245 (1846).

² *Compt. rend.*, 95, 36 and 137 (1882).

³ *Loc. cit.*

⁴ *Lehrbuch*, 4 Aufl., 4, 562 (1836).

⁵ *Compt. rend.*, 125, 948 (1897).

⁶ *Ibid.*, 136, 504 (1903).

⁷ *Ibid.*, 144, 14 (1908).

⁸ *Ber.*, 36, 128 (1909).

⁹ *Compt. rend.*, 148, 1105 (1908).

¹⁰ *Ibid.*, 144, 199 (1907).

resulting from reduction of cupric acetate in ammoniacal solution with hydroxylamine sulfate. Ammoniated cuprous formate, $\text{Cu}_2(\text{HCO}_2)_2 \cdot 4\text{NH}_3 \cdot 1/2\text{H}_2\text{O}$, and ammoniated cuprous benzoate, $\text{Cu}_2(\text{C}_7\text{H}_5\text{O}_2)_2 \cdot 5\text{NH}_3$, were prepared by Joannis¹ by the action of the ammonium salts of the respective acids on cuprous oxide—both reagents in liquid ammonia solution.

Experimental.

The cuprous salts of some organic acids were desired for purposes which, if accomplished, will be reported later, and an attempt was made to prepare the oxalate by reducing the cupric compound with sulfur dioxide in the presence of oxalic acid or of alkali oxalate. No change could be obtained, possibly on account of the very slight solubility of the cupric oxalate, but, when the latter was dissolved in ammonia and sulfur dioxide was passed in to acid reaction, some interesting color changes and precipitations took place, and there was left an insoluble mixture containing a brown substance now believed to be the desired salt. This procedure was not studied, since a new and simpler process was found.

Cuprous sulfite was sprinkled little by little into a hot solution of an excess of oxalic acid; the solid changed from bright red to brown and much sulfur dioxide was evolved. The precipitate was almost as fine and difficult to filter as calcium oxalate, but became coarser by continued warming. It was filtered off, washed with water and finally with alcohol and tested qualitatively, as follows:

1. Hydrochloric acid, diluted (1:2), was freed from dissolved oxygen by warming in a stream of carbon dioxide and a little of the compound was thrown into the hot acid while still protected from air by the stream of gas. Immediate solution took place, indicating absence of free copper and only a faint color was present, indicating absence of cupric salt.

2. The compound dissolved in concentrated ammonia with considerable blue color which rapidly increased in intensity; that there was no free copper in the substance was proven by the absence of insoluble residue.

3. Warm dilute (1:15) nitric acid used in small quantity decomposes the substance, forming copper and copper nitrate. The solution, freed from copper by hydrogen sulfide, showed the presence of oxalic acid in large quantity.

4. Decomposed with a few drops of concentrated nitric acid and dissolved in water, the solution gave no precipitate with barium chloride, showing absence of sulfur compounds.

5. With cold, very dilute, sulfuric acid the compound remains unchanged, but it decomposes instantly on warming to about 30°, giving cupric oxalate and copper.

¹ *Compt. rend.*, 138, 1499 (1904).

6. Dilute nitric acid (1:15) does not change it in the cold but oxidizes it to copper nitrate by heating.

7. A sample of about 2 g. was heated in a water-jacketed air bath (about 95°) for two hours and changed in color to a dull, dark gray. This substance, when thrown into cold dilute nitric acid, changed back to the brown without any green or blue color showing in the liquid or in the solid.

8. Heated alone in a crucible, the substance changes to gray, then to greenish gray giving off traces of water, and then decomposes suddenly, almost explosively, scattering so that no residue remains in the crucible. (Silver oxalate explodes if heated quickly.¹)

Quantitative determination of the copper was made by decomposing it in a crucible with a few drops of slightly diluted nitric acid, evaporating and igniting.

0.3393 and 0.3003 g. gave 0.2148 and 0.1911 g. CuO; found: 50.57 and 50.82% Cu; Calc. for $\text{Cu}_2\text{C}_2\text{O}_4$: Cu, 53.89%; for $\text{Cu}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$: Cu, 50.61%.

The gray sample mentioned above was analyzed with the results:

0.1132 and 0.1317 g. gave 0.0717 and 0.0872 g. CuO; found: 50.70% and 50.82% Cu.

From this, taken in connection with its behavior with dilute nitric acid, the gray substance is of the same composition as the brown.

Attempts were made to find the reducing value of the oxalic acid radical by suspending the substance in hot water, passing hydrogen sulfide through and gradually adding dilute hydrochloric acid. The excess hydrogen sulfide was removed from the filtrate by heating in a stream of carbon dioxide and the solution was titrated with permanganate. Sharp end points were obtained, but the results were very erratic, all of them, however, indicating much greater reducing power than calculated for the formula $\text{Cu}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, or even for the anhydrous salt formula. The substance was then decomposed in the presence of an excess of calcium nitrate with dilute nitric acid, and calcium oxalate was precipitated with an excess of ammonia. The oxalate was then titrated as usual.

The factor for the permanganate was $\text{cc.} \times 1.0967 = \text{cc. } 0.1 \text{ N.}$ 0.2339 and 0.2107 g. required 23.14 and 20.85 cc.; found: 47.53% and 47.55% C_2O_4 .

The complete analysis, as far as carried out, is Cu 50.69, C_2O_4 47.54; Calc. for $\text{Cu}_2\text{H}_2(\text{C}_2\text{O}_4)_4$: 51.14, 47.25.

A hot water extract of the salt was found to be acid to methyl orange, though this may have been due to hydrolysis rather than to acidity of the salt.

What is apparently the same substance can also be prepared by digesting cuprous oxide with a solution of two and one-half parts of oxalic

¹ Richter's "Organic Chemistry," 3^d Am. Ed., Vol. I, 433-4.

acid. A sample made by digesting 4 g. of the oxide with the acid for three hours was analyzed for copper:

0.2256 g. gave 0.1156 g. CuO; found: Cu 50.95%.

The reactions of many other organic acids on cuprous sulfite have been tried but, in all cases, more or less green coloration has indicated the formation of cupric compounds. Apparently, the solubility of the cuprous compound first formed is chiefly responsible for the success of the experiment. The appearance of the insoluble portions obtained in some of the experiments gives encouragement to the hope that they can be used for further transformations as cuprous salts.

Conclusions.

1. Attention has been called to an erroneous statement common in text-books of general chemistry.
2. A new method for the preparation of cuprous salts of oxygen acids has been devised, and the probable conditions of its applicability have been indicated.
3. A new compound of the class has been prepared, some of its properties described, and its probable formula determined.

LEXINGTON, KY.

[HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK CITY.]

A PRECIPITANT FOR AMMONIA. (A SUBSTITUTE FOR NESSLER'S REAGENT.)

By SARA STOWELL GRAVES.

Received March 3, 1915.

TABLE OF CONTENTS.—I. Introduction. II. The Reagent. III. Results with Reagent. IV. Directions. V. Applications. VI. Summary.

I. Introduction.

Nessler's reagent for ammonia, developed in the early part of the last century, was applied to water analysis in 1867. It has stood the test of time and has come into wide use, particularly in physiological work. But with the development of colorimetry, its disadvantages, as well as its value, have become apparent and innumerable modifications of the reagent have resulted. Its instability and tendency to produce a cloud in dilute solutions are the chief difficulties. Recently efforts have been made to apply the reagent in micro-Kjeldahl¹ work (without previous distillation) with varying degrees of success, the precipitate due to salts making the accurate matching of colors extremely hard.

A probable explanation of why the colored solution produced by Nessler's reagent becomes cloudy, especially in the presence of salts, may be found in the following considerations:

¹ Folin and Farmer, *J. Biol. Chem.*, 11, 493 (1912); Gulick, *Ibid.*, 18, (1914); Bock and Benedict, *Ibid.*, 20, 47 (1914).

(a) Only the iodide complex of mercury and ammonia is highly colored and soluble.

(b) The other complexes of mercury and ammonia, like the chloride described in this paper, are colorless, insoluble compounds.

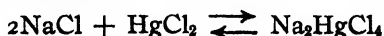
Therefore in the presence of other salts, the colored iodide complex is probably partially changed to, and in equilibrium with, the colorless complexes, such as the chloride or sulfate, and as only the color is estimated, appreciable error may result.

The idea of finding a precipitant for ammonia, was suggested by a research of Dr. W. G. Lyle as to the possibility of determining the non-protein nitrogen in blood, nephelometrically, and in the course of discussion, mercuric chloride was mentioned as a likely reagent.

Having in mind Nessler's solution and its disadvantages, an attempt was made to evolve an alkaline mercuric chloride solution which would be stable and colorless and which would form a white precipitate with ammonia, quantitatively. Since the salts, which interfere with the Nessler color, produce a white complex with mercury and ammonia, no probable error would be introduced by this proposed reagent.

II. Reagent.

Mercuric Chloride Complexes.—When a solution of mercuric chloride is made alkaline, immediately the yellow or red oxide forms, but it was found that by first adding sodium chloride, a complex was formed which was stable except in the presence of a large excess of alkali. As will be seen from the following equation, 2 molecules of sodium chloride unite with one of mercuric chloride:



This complex is readily soluble in water and while it has an appreciable dissociation into HgCl_2 and NaCl ,¹ with large amounts of sodium chloride, the dissociation is practically zero. It has the further advantage that chlorine compounds are more stable than those of the other halogens. Thus, the ammonium complexes of mercuric chloride are more stable than those of the bromide or iodide. The neutral iodine complex has a noticeable vapor tension of ammonia, which the analogous complex of chlorine has not.

Components of Reagent.—The reagent used consisted of mercuric chloride, sodium chloride, and lithium carbonate. The latter was chosen because of the low atomic weight of the cation and, therefore, but slight tendency to cause agglutination of suspensoids. Each component of the reagent was varied, in order to ascertain the most favorable conditions for the quantitative precipitation of ammonia.

¹ W. Richards and Archibald, *Z. physik. Chem.*, 40, 385 (1902); Le Blanc and Noyes, *Ibid.*, 6, 393 (1890).

50 cc. of a cold saturated solution of mercuric chloride and 50 cc. of water were chosen arbitrarily and the sodium chloride and lithium carbonate varied to the points at which mercuric oxide formed—with the following results:

TABLE I.—PRECIPITATION POINTS OF MERCURIC OXIDE.

| Sat. sol. of HgCl ₂ . Cc. | H ₂ O. Cc. | NaCl. Grams. | Saturated Li ₂ CO ₃ solution. Cc. |
|---|-----------------------|-----------------|---|
| 50 | 50 | 5 | 5 |
| 50 | 50 | 10 | 30 |
| 50 | 50 | 15 | 50 plus |
| 50 | 50 | 20 | 50 plus |

50 cc. of mercuric chloride solution, 15 g. of sodium chloride, 35 cc. of saturated lithium carbonate solution, and 65 cc. of water were found to produce a satisfactory reagent. Experiments showed that it is fully as sensitive as Nessler's reagent, and it seemed likely that, owing to the sensitiveness of nephelometry, very small amounts of ammonia could be determined quantitatively more easily as a cloud than as a very faint color. The reagent precipitates ammonia from ammonium sulfate solutions as dilute as 1 part per million, producing a bluish white cloud which agglutinates in stronger solutions after a few minutes.

Before studying the reagent further it was necessary to find a protective colloid, to keep the precipitate in suspension long enough to make nephelometric readings (10–30 minutes). Soluble starch, when very dilute, proved satisfactory.

Two sets of experiments were accordingly carried out, using 10 cc. of ammonium sulfate solution (10.0 mg. per liter), 15 cc. of starch solution (5.0 mg. per liter) and 5 cc. of reagent, in which the mercuric chloride and lithium carbonate were varied. The clouds formed were compared with a fixed standard, in the nephelometer.

(1) **Mercuric Chloride.**—The mercuric chloride was varied from 25 to 75 cc. of saturated solution per 150 cc. of reagent. There was no appreciable change in the readings of the different solutions tested.

(2) **Lithium Carbonate.**—The amount of saturated solution of lithium carbonate (about 1%) was varied from 12.5 to 75 cc. 65 to 75 cc. produced mercuric oxide on standing. Solutions containing less than 65 cc. showed no marked difference in nephelometric readings.

Protective Colloid.—The effect of starch upon salt was studied in two connections: (1) When the reagent contained varying amounts of sodium chloride. (2) When the ammonia solutions contained varying amounts of potassium sulfate, thus allowing for any reasonable variation in the amount of ammonia as compared to salt found in micro-analysis.

(1) To 150 cc. of reagent, which already contained 15 g. of sodium chloride, more sodium chloride was added in varying amounts of 10,

20, 25, and 35 g., respectively. It was found that the solutions containing 20, 25 and 35 g. additional salt all allowed the use of a fairly large amount of starch. 25 g. were then decided upon, making a total of 40 g. of sodium chloride in 150 cc. of reagent. Later experiments show the effect of sodium chloride upon the constants of the reagent.

(2) The ammonium sulfate solutions were of three types: *A*, pure. *B*, with the amount of potassium sulfate found in normal Kjeldahl work. *C*, with four times the amount of salt found in normal Kjeldahl work.

Solution A contained 1.0 mg. of ammonium sulfate in 100 cc. or 2.57 mg. of ammonia per liter.

Solution B contained 1.0 mg. of ammonium sulfate, and 10 cc. of potassium sulfate solution (75 g. per liter), in 100 cc.

Solution C contained 1.0 mg. of ammonium sulfate, and 40 cc. of potassium sulfate solution (75 g. per liter) in 100 cc.

To solutions *A*₁, *B*₁, and *C*₁ (10 cc.) were added various amounts of starch, always diluting to 25 cc. at this point, and the time was determined from the moment the reagent (5 cc.) was added, until agglutinations were visible to the naked eye. At the same time it was observed that the nephelometric readings became slightly higher. The results obtained are seen in Table II, the minutes indicating the time during which the solutions are constant and suitable for nephelometric work, and the concentration of starch indicating the strength of the final solutions:

TABLE II.—TIME OF AGGLUTINATION.

| Concentration starch. Mg. per liter. | <i>A</i> ₁ . Min. | <i>B</i> ₁ . Min. | <i>C</i> ₁ . Min. |
|---|---------------------------------|---------------------------------|---------------------------------|
| 0 | 14 | 11 | 5 |
| 2.5 | 27 | 15 | 6 |
| 5 | 37 | 25 | 10 |
| 10 | 48 | 40 | 14 |
| 15 | 60 | 60 | 20 |
| 20 | .. | .. | 28 |
| 25 | .. | .. | 32 |
| 40 | .. | .. | 50 |
| 50 | .. | .. | 60 |

It may be seen that the suspensions are fairly stable even without starch.

Completeness of Precipitation.—It was necessary to determine whether or not the completeness of precipitation was affected by the colloid.

To do this, solutions *A*₂, *B*₂, and *C*₂ were prepared containing 0.500 mg. of ammonium sulfate instead of 1 mg. as in *A*₁, *B*₁, and *C*₁. To 10 cc. of solutions *A*₂, *B*₂ and *C*₂ were added definite amounts of starch, diluting at this point to 25 cc. and finally 5 cc. of reagent were added with shaking, and the solutions compared with solutions *A*₁, *B*₁, and *C*₁, respectively, in the nephelometer. From the results the nephelometric constants

(*k*) were calculated, using the formula¹

¹ For details as to nephelometric instrument, formula and manipulations, see Kober, *J. Biol. Chem.*, 13, 490 (1913).

$$y = s/x - (1-x)sk/x^2$$

where y equals the reading of A_2

" s " " " " A_1

" x " " ratio of A_1 to A_2 or 0.500.

Using the reagent containing 40 g. of sodium chloride per 150 cc., the following constants were obtained:

TABLE III.—EFFECT OF STARCH ON NEPHELOMETRIC CONSTANTS.

| Concentration of starch. Mg. per liter. | A/k. | B/k. | C/k. |
|--|-------|-------|-------|
| 50 | 0.033 | 0.140 | 0.138 |
| 35 | 0.075 | 0.135 | 0.132 |
| 25 | 0.130 | 0.136 | 0.136 |
| 15 | 0.133 | 0.138 | 0.136 |
| 5 | 0.140 | 0.132 | 0.133 |

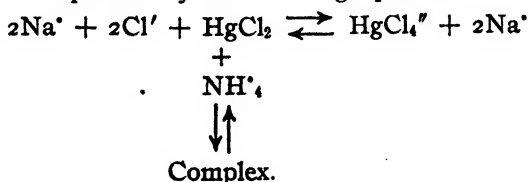
The above results show that in starch solutions containing 35 and 50 mg. per liter the precipitation of the pure solutions A, is retarded, but that in solutions containing less than 35 g. per liter the precipitation of the three solutions is apparently complete.

Table IV shows the effect of a reagent containing only 15 g. of sodium chloride per 150 cc. under similar conditions.

TABLE IV (Continuation of III).

| Concentration of starch. Mg. per liter. | A/k. | B/k. | C/k. |
|--|----------|----------|-------|
| 15.0 | Negative | Negative | 0.077 |
| 5.0 | 0.090 | 0.180 | 0.173 |
| 2.5 | 0.164 | 0.154 | 0.166 |

Here it is evident that the precipitation is delayed in a starch solution containing 15 mg. per liter. The slightly higher constants with this reagent might be explained by the following equation:

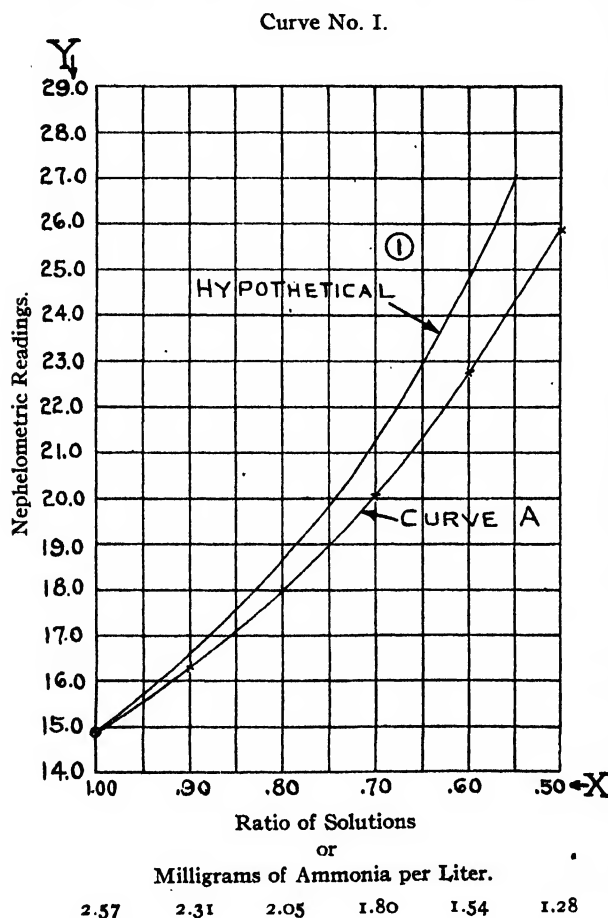


According to the Law of Mass action the increased amount of sodium chloride would have a tendency to shift the equilibrium from the ammonium complex formation and therefore the reagent containing less sodium chloride might give more complete precipitation and thus slightly higher nephelometric constants.

III. Results with Reagent.

To test the precipitability of ammonia by the modified mercuric chloride reagent, three sets of ammonium sulfate solutions A, B, and C were made, as previously described, in which the amount of ammonium sulfate was varied from 10 to 5 mg. per liter.

Starch was added, the ammonia precipitated by the reagent, and the solution compared with a known standard in the nephelometer. From



the readings (usually 2) the accompanying curves were plotted. They are compared with the hypothetical or colorimetric curves. Curve No. I, with solutions A; Curve No. II, with solutions B; Curve No. III, with solutions C.

Solutions A contained 10 cc. of ammonium sulfate solutions containing 100, 90, 80, 70, 60, 50 mg. per liter, made up to 100 cc. with ammonia-free

Solutions B contained ammonium sulfate in the same amounts as solutions A, and in addition 10 cc. of potassium sulfate solution (75 g. per liter); the volume was then made up to 100 cc. with ammonia-free water.

TABLE V.—NEPHELOMETRIC READINGS.

| (NH ₄) ₂ SO ₄ Mg. per liter. | Solutions A. | | Solutions B. | | Solutions C. | |
|--|------------------|-----------------|------------------|-----------------|------------------|-----------------|
| | Readings. Mm. | Constant. k. | Readings. Mm. | Constant. k. | Readings. Mm. | Constant. k. |
| 10.0 | 14.90 | ... | 14.90 | ... | 14.90 | ... |
| 9.0 | 16.30 | 0.140 | 16.30 | 0.140 | 16.30 | 0.140 |
| 8.0 | 17.95 | 0.141 | 17.90 | 0.152 | 17.93 | 0.146 |
| 7.0 | 20.05 | 0.140 | 20.06 | 0.139 | 20.00 | 0.145 |
| 6.0 | 22.75 | 0.131 | 22.80 | 0.128 | 22.77 | 0.136 |
| 5.0 | 25.80 | 0.134 | 25.85 | 0.132 | 25.85 | 0.132 |
| Average, | | 0.137 | | | 0.138 | 0.140 |

¹ The hypothetical or colorimetric curve is obtained by assuming the readings to be inversely proportional to the concentration of the substance.

Solutions C were like solutions B except that they contained 40 cc. instead of 10 cc. of potassium sulfate solution (75 g. per liter).

To 10 cc. of solution were added 15 cc. of starch solution (30 mg. per liter) and finally, while shaking in a rotary fashion, 5 cc. of reagent were run in from a pipet. The strongest solution (10 mg. per liter) of a series was used as a standard, and the others of a series compared with it in succession. The preceding readings are the average of 2 or 3 readings.

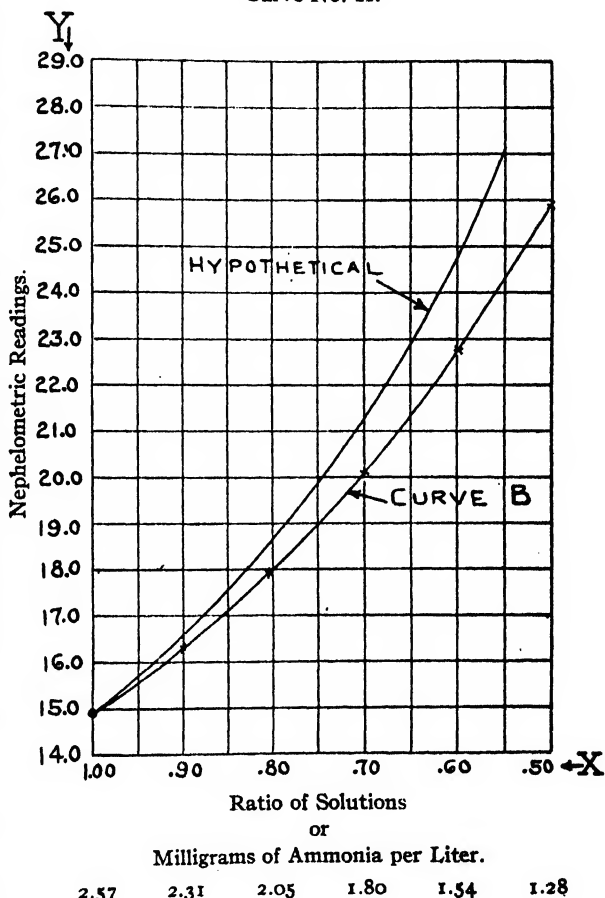
From these results it seems probable that the precipitation is nearly complete, since:

(1) The curves are well below the hypothetical.

(2) The readings are consistent.

(3) The nephelometric constants are in close agreement.

Curve No. II.



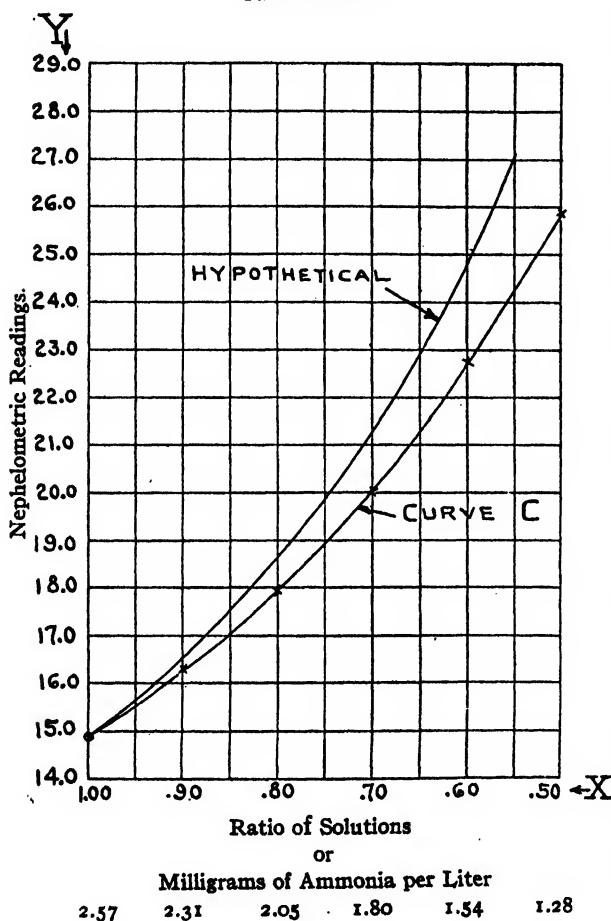
IV. Directions.

A. Solutions: Ammonia-free Water.—Ammonia-free water must be used in making up all solutions which enter into the standard solution, just as with the Nessler standard. The usual recommendation is water which contains not more than 0.005 mg. of ammonia in 100 cc. This may be easily obtained by distilling tap water which has been made slightly acid with sulfuric acid.

Reagent.—To 80 g. of sodium chloride are added 130 cc. of water and 100 cc. of a cold saturated solution of mercuric chloride, with shaking. When the salt is practically all dissolved, 70 cc. of a saturated solution of lithium carbonate (1%) is added slowly while shaking, so that no

mercuric oxide forms on the sides of the flask. The solution is usually cloudy, owing to the ammonia in the reagents, but if well shaken with

Curve No. III.



talcum powder (3-5 g.) it is easily filtered clear. The solution may be used at once, or if carefully stoppered may be kept almost any length of time.¹ Filtering the reagent does away with errors due to impurities in its constituents.

Protective Colloid.

—A stock solution of starch is freshly made each day by boiling 1 g. of starch in ammonia-free water until clear and making up to 100 cc. with ammonia-free water.

Standard Solution.

—Ammonium sulfate prepared and purified according to Folin's² directions is used for a standard. The standard solution is made by taking 10 cc. of an ammonium sulfate

solution (100 mg. per liter), adding 10 cc. of potassium sulfate solution (75 g. per liter) and making up to 100 cc. in a volumetric flask with ammonia-free water. The amount chosen for a standard cloud is usually 10 cc. of this solution, ammonium sulfate (10 mg. per liter) to which is added 15 cc. of 0.003% starch and 5 cc. of reagent. Half or even one-fourth of the above amount is ample, the object in choosing a fairly strong standard being to lessen the percentage of error due to traces of ammonia in dust or water. In all experiments controls should be made on the water as well as on the reagents.

¹ Solutions have been kept several weeks without noticeable change.

² *Loc. cit.*

Potassium sulfate is added to the standard solutions in order to reproduce as far as possible the conditions found in all Kjeldahl work. Preceding data show that large or small amounts of salt do not affect the precipitation of ammonia with the reagents as given.

(B) Kjeldahl Nitrogen Estimation.

Catalyst.—It is necessary to use mercuric oxide instead of cupric sulfate as a catalytic agent, owing to the blue color developed by copper in alkaline solution.

Dilution.—After the usual heating the solutions containing the substance are diluted to 500 cc. and the blanks to 250 cc. These solutions may be designated as solutions A_x and A_y .

Neutralization.—5 cc. or more of solution A_x and 50 cc. or more of solution A_y are neutralized with sodium hydroxide, using litmus paper as indicator and each is made up to 100 cc. in a volumetric flask with ammonia-free water. Designation, solutions B_x and B_y .

To 5 cc. of solution A_x is added about 5 cc. 1 *N* sodium hydroxide and then 1 *N* sodium hydroxide drop by drop to the neutral point. To 50 cc. of solution A_y is added about 30 cc. of 15% NaOH and then 1 *N* NaOH drop by drop to the neutral point.

Care must be taken not to add a considerable excess of sodium hydroxide, or else mercuric oxide will form upon addition of the reagent. The small amounts of ammonia in the control can be readily estimated, if the control solution is not more than one-twentieth as dilute as the solution containing the substance. If the solutions B are cloudy because of the precipitation of alkaline earths, etc., they should be filtered through a dry filter after making up to volume.

Precipitation.—To 10 cc. of solution B are added 16 cc. of starch solution (30 mg. per liter) and 5 cc. of reagent with shaking, and the cloud produced compared with a standard ammonium sulfate cloud, by means of the nephelometer.

Calculation of Results.—From the readings of the standard solution and the unknown, by means of the formula $y = s/x - (1-x)sk/x^2$ the ratio of the concentrations of the solutions can be found and the amount of ammonia or nitrogen in the substance taken for analysis readily calculated, subtracting the amount of ammonia in the control. A more convenient form of the equation when solving for x is $x = \frac{s + sk + \sqrt{(s + sk)^2 - 4sky}}{2y}$ in which $(s + sk)$ is constant throughout any series of determinations. For this reagent k is about 0.138.

V. Applications.

The preceding method of making nitrogen estimations was tried on ammonium sulfate alone, and on ammonium sulfate with organic matter

(filter paper), as well as on uric acid and urine, with satisfactory results—which attest to the sensitivity of the reagent and its ability to precipitate ammonia quantitatively.

(1) 0.1001 g. of ammonium sulfate was digested with 5 g. of potassium sulfate and 20 cc. of sulfuric acid in the usual way. Duplicate estimations as well as duplicate controls were made. The solutions were diluted directly *without the usual distillation*, and the ammonia was determined according to the preceding directions, the standard solution containing 0.1001 g. of ammonium sulfate.

| Solution. | Y. | S. | X. | Nitrogen found, g. | % Nitrogen found. | % Nitrogen theoretical. |
|----------------------------|-------|-----------------|-------|--------------------|-------------------|-------------------------|
| I..... | 13.75 | 13.96 | 1.016 | 0.02150 | 21.24 | 21.15 |
| II..... | 13.72 | 13.96 | 1.018 | 0.02155 | 21.29 | 21.15 |
| | | $\frac{1}{2}$ S | | | | |
| Control ¹ | 25.43 | 13.96 | 0.483 | 0.00024 | ... | ... |

(2) The above experiment was repeated with the difference that one sheet of purest filter paper (7 cm.) was digested in each flask in lieu of organic matter.

| Solution. | Y. | S. | X. | Nitrogen found, g. | % Nitrogen found. | % Nitrogen theoretical. |
|----------------------------|-------|-----------------|-------|--------------------|-------------------|-------------------------|
| I..... | 13.82 | 14.00 | 1.014 | 0.02145 | 21.18 | 21.15 |
| II..... | 13.80 | 14.00 | 1.015 | 0.02150 | 21.23 | 21.15 |
| | | $\frac{1}{2}$ S | | | | |
| Control ¹ | 24.00 | 14.00 | 0.503 | 0.00025 | ... | ... |

(3) 0.100 g. uric acid was digested in each of four experiments with 10 g. of potassium sulfate and 20 cc. of concentrated sulfuric acid in the usual way. Two controls were made at the same time.

Two of the uric acid digestions and one control were distilled by the aeration method² and the ammonia was estimated by titrating the distillate. The other two digestions and a control were treated as in Experiments 1 and 2.

PERCENTAGE OF NITROGEN IN URIC ACID.

| No. | Found by aeration method. | Found by new method. | Theoretical. |
|---------|---------------------------|----------------------|--------------|
| I..... | 32.62 | 32.90 | 33.33 |
| II..... | 32.60 | 32.95 | 33.33 |

No attempt was made to purify or dry the substance, which may well have contained 1% of moisture.

(4) Experiment 3 was repeated, replacing the uric acid by 5 cc. of urine, with the following results: (urine was diluted with an equal volume of 0.2% tricesol).

¹ See solutions under *neutralization* marked A₂ and B₂. $\frac{1}{2}$ S indicates one-half as strong as standard solution (which see).

² E. A. Kober and S. S. Graves, *THIS JOURNAL*, 35, 1546 (1913).

PERCENTAGE OF NITROGEN IN URINE.

| No. | Found by aeration method. | Found by new method. | (A mixed specimen of normal urine.) |
|---------|---------------------------------|----------------------------|---|
| I..... | 0.960 | 0.952 | ... |
| II..... | 0.976 | 0.948 | ... |

VI. Summary.

A new reagent for ammonia has been found which:

- (1) Is more stable than Nessler's reagent in the presence of salts.
- (2) Is fully as sensitive as Nessler's reagent.
- (3) Will precipitate ammonia quantitatively.
- (4) Will give accurate results nephelometrically.
- (5) May be useful in water analysis.
- (6) May be directly applied to normal- and micro-Kjeldahl determinations, thus doing away with the tedium and errors of distillation.

I desire to express my gratitude to Mr. P. A. Kober, for the opportunity of working out this problem.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON.]

THE USE OF THE INTERFEROMETER FOR THE ANALYSIS OF SOLUTIONS.

By LEASON H. ADAMS.

Received March 29, 1915.

Chemists have long used the refractometer as an aid in analytical work, but have not made use of the interferometer to the extent that its precision and general convenience would warrant. The use of the ordinary forms of refractometer is limited by the circumstance that the change of refractive index with temperature is usually such as to require regulation of temperature to 0.01° in order to secure an accuracy of one unit in the sixth place in the measurement of refractive index. By means of the interferometer, on the other hand, it is a simple matter, requiring no special regulation of temperature, to secure an accuracy of one unit in the seventh place; this is possible because in the latter case we are comparing the refringence of one liquid (or gas) with that of another of very nearly the same composition and hence possessing almost the same temperature coefficient of refringence. In other words, with the refractometer one can determine the composition of a solution to 2 parts in 10,000 of solvent, but with the interferometer—provided that certain simple precautions be observed—to 2 parts in a million. The interferometer is adapted to the determination in any transparent mixture of a single varying component; this component may be solute or solvent, electrolyte or nonelectrolyte, indeed any substance which will not attack the

instrument. It is the purpose of the present paper to describe briefly a commercial interferometer which is convenient for chemical purposes, to discuss its mode of operation and to point out means of rendering it more generally useful. In the first place it is desirable, in the interest of a better understanding of the use of the interferometer, to recall some fundamental facts concerning the interference of light waves.

Principle of the Interferometer.—All interferometers, when reduced to their simplest terms, may be represented by Fig. 1. Light from a source, S , passes through two small openings, R_1 and R_2 , and the two

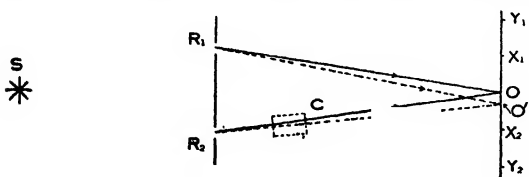


Fig. 1.—Elementary Interferometer. Two beams of light from a source, S , pass through the rectangular openings R_1 R_2 and falling on the screen at right produce a system of interference fringes which by the introduction of material at C are shifted by a certain amount depending on the thickness and refractive index of the material.

beams overlap as they fall on the screen at the right. At a point, O , equidistant from R_1 and R_2 the light waves arrive in the same phase, and a light spot or band results; but at all other points on the screen the paths of the two beams are of different lengths. Thus at X_1 or X_2 , this path difference is exactly one-half wave-length, the two beams

"interfere" and a dark band results; at Y_1 or Y_2 the retardation is a whole wave-length, the two sets of waves arrive at the screen again in the same phase, and a bright band is observed. In this way there is formed on the screen a series of alternate bright and dark bands, or so-called interference fringes.

With monochromatic light as the source (*e. g.*, the light from a sodium flame) the bands are alternately black and the color of the light source (*e. g.*, yellow); with white light, on the other hand, only the central band is pure white, the next bright band beyond the adjacent dark spaces being edged with blue toward the center of the system and with red on the outside, while the bands still further away from the center appear successively more and more diffusely colored, finally fading into a uniform white.

Now if any material is placed in the path of one beam, as at C , the light waves of this beam will be retarded by an amount depending on both the thickness and refractive index of the material. The optical path is therefore lengthened, the expression for the path difference p being

$$p = l(n - n_0) \quad (I)$$

where l is the thickness and n the refractive index of the material and n_0 that of the surrounding medium. Since the optical path R_2O has now been lengthened, the two trains of light waves arrive in the same

phase no longer at O but at another point O' ; the central bright band originally at O is therefore displaced to the point (O') which is optically equidistant from R_1 and R_2 . Furthermore, it can readily be shown that for light of wave-length λ the number of fringes between O and O' —that is, the displacement of O measured in fringes (each made up of one bright and one dark band)—follows the simple relation,

$$N = p/\lambda,$$

whence by (I)

$$N = l(n - n_0)/\lambda \quad (\text{II})$$

Therefore, by counting the number of fringes, we may determine the product $l(n - n_0)$ and hence either the thickness or the difference in refractive index if the other is known.

Again, it is evident that by inserting a plate in the path of each beam, we can in this way determine the difference in refractive index of the two plates, if the thickness of each is known. Likewise, if we have a pair of similar vessels of appropriate construction, place one in the path of each beam, and observe the displacement of O (in terms of fringes) consequent upon the filling of each vessel with a transparent substance (or mixture), we can by this means determine the difference in refractive index of the two substances. Such an arrangement constitutes a differential refractometer, which is capable of giving with a very high degree of accuracy the difference of refractive index of any two mixtures (or pure substances, liquid or gaseous); and this difference can be utilized as a convenient and accurate measure of the concentration of a single varying component in a solution (or gaseous mixture). A convenient instrument designed for this purpose is the Zeiss Water Interferometer,¹ the essential features of which we proceed to outline.

Description of the Zeiss Interferometer and of Its Mode of Operation.

—The simplified interferometer shown in Fig. 1 would be inconvenient in practice; a more useful arrangement is that of Fig. 2, which illustrates the set-up first used by Rayleigh, and later embodied with slight modifications in the apparatus made by Zeiss. White light from a slit is made parallel by a collimating lens, L (Fig. 2a), passes through the two rectangular openings $R_1 R_2$ as two beams which unite at O , forming a system of interference fringes which are viewed with a suitable eye-piece (not shown in this figure). Two similar chambers, $C_1 C_2$, of appropriate construction are placed, one in each light path; the displacement of the fringes caused by a difference in refractive index of their contents is com-

¹ Made by Carl Zeiss, Jena. Full details of the construction of this instrument may be found in papers by Löwe (*Z. Instrumentenkunde*, 1910, 321), by Haber and Löwe (*Z. angew. Chem.*, 23, 1393 (1910)) and in the descriptive literature published by the Zeiss firm.

pensated—*i. e.*, the central bright fringe is brought back to the zero position—by tilting the inclined glass plate P_1 , P_2 being fixed.

This tilting changes the effective thickness of the compensating plate P_1 ; when the central bright fringe is restored to the zero position, the change in effective thickness of the compensator just neutralizes the difference in the optical path through C_1 and C_2 . This arrangement is

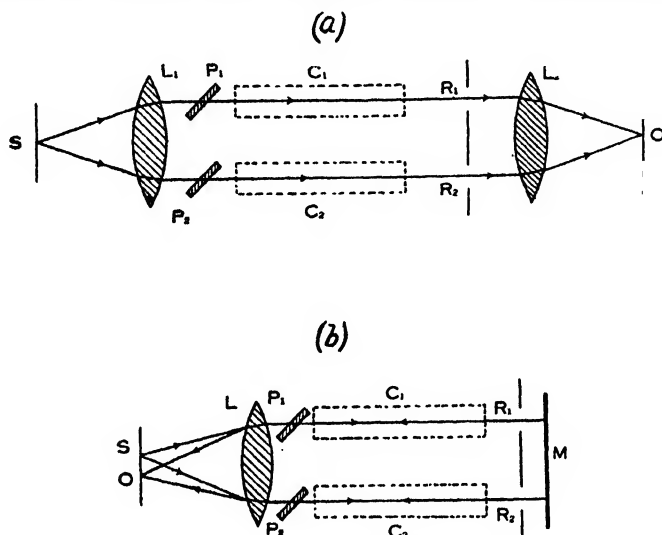


Fig. 2.—Diagram of arrangements of interferometer; the two interfering beams are separated and reunited in (a) by two lenses, in (b) by a single lens.

essentially that used in the Zeiss Laboratory Interferometer (for gases); for the sake of compactness and portability it is modified slightly in the Water Interferometer and Portable Gas Interferometer. In this modification, illustrated in Fig. 2b, the same lens serves the double purpose of separating and reuniting the two interfering beams.

The actual arrangement of the Water Interferometer is shown in some detail in Fig. 3, which is a diagram in plan and elevation of the instrument in use here.

White light is furnished by the small 4 volt tungsten lamp F . By means of the lens A , a mirror and the totally reflecting prism K , the image of the filament F is focused on the narrow slit S (see Fig. 3, lower half); this slit acts as a (very narrow) secondary source, the light from which is rendered parallel (just as in Fig. 2b) by the lens L . The light then passes through the two compartments C_1 C_2 of the water chamber and the rectangular apertures R_1 R_2 , thence to a mirror, M , where the two beams of light are reflected back upon themselves, pass through the water chamber again and finally, by means of the lens L , are reunited at O ,

forming a series of interference fringes. These fringes are viewed by the cylindrical ocular *E*, which gives a magnification of 50 diameters, but in the horizontal direction only; the reasons for the use of a cylindrical ocular will be referred to later.

Besides the two interfering beams of light already considered, another pair proceed from the slit *S* in a precisely similar way, except that they pass *below* and not through the chamber *C*, likewise forming at *O* a second system of interference fringes. This latter fringe system is (practically) fixed in position; its sole purpose is to furnish a set of fiduciary lines

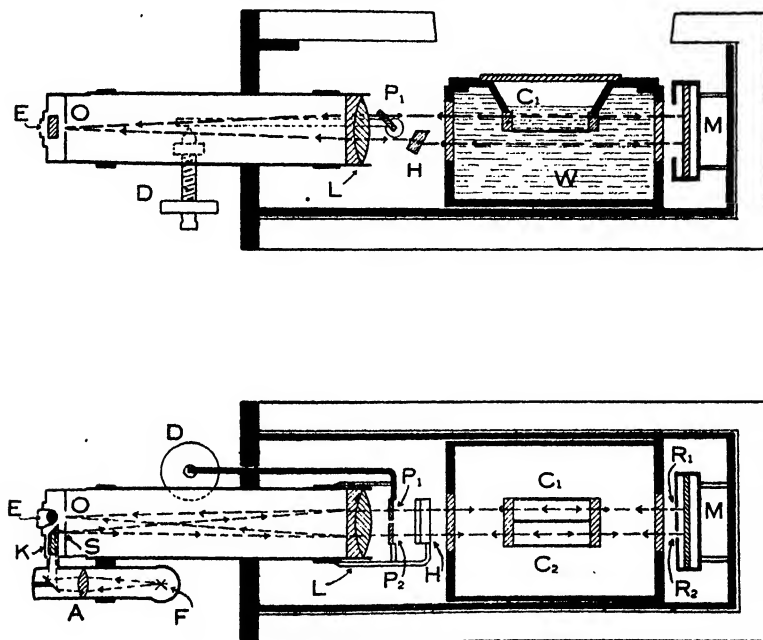


Fig. 3.—Drawing in plan (below) and elevation (above) of the Zeiss Water Interferometer.

which take the place of the cross-hairs ordinarily used as reference marks in optical instruments. Accordingly, if the eye is placed at *E*, one sees two sets of alternate bright and dark bands, the two sets being separated by a narrow horizontal dark line.¹ In each set of fringes only one of the bright bands is pure white, and the bands adjacent to it are bordered with blue towards the center and with red on the outside; it is this central

¹ The width of this line is made very small by means of the auxiliary plate *H*. Furthermore, the cylindrical eye-piece by magnifying only in horizontal direction does not increase the apparent thickness of the horizontal line. This feature of the cylindrical ocular is quite apart from its further advantage of giving, for a 50 diameter magnification, 50 times more light than an ordinary magnifier of the same power.

achromatic band (or the black bands immediately adjacent to it) which constitute the reference point of each system.

The upper set of bands can be displaced relatively to the lower set by tilting the movable inclined plate P_1 (P_2 is fixed); this is effected by turning the micrometer screw with attached drum D , by means of which, therefore, the two achromatic bands can be brought to coincidence, and the corresponding reading on the drum observed. Now, by placing one liquid (*e. g.*, pure water) in compartment C_2 and a second (*e. g.*, a dilute salt solution) in C_1 , the upper set of bands is displaced to the left; but they can be restored to their original position by turning the drum D in the proper direction. When an exact match is again obtained—*i. e.*, when the achromatic fringe is brought to a position directly above that of the corresponding fringe of the fixed lower system—the drum reading is again observed; a series of such settings can be made which will differ by no more than 1 division on the drum (which corresponds to about one-twentieth of a band or to 2 parts solute per million of water). The reading is a measure of the difference in refractive index of solution and water, and hence a measure of the concentration of the solution in C_1 . The interpretation of the readings in terms of actual concentration will now be treated.

Analysis of Solutions.—Since with the interferometer we determine a single variable, namely a difference in refractive index—or rather, an arbitrary reading related to it—it is evident that its utility for the analysis of solutions is limited to (1) the determination of the concentrations of a single substance in (*a*) a given liquid or (*b*) a mixture of liquids, or of liquids and solids, of constant composition; (2) the determination of the concentration of a solution containing several solids in fixed proportion (*e. g.*, sea water); and (3) the analysis of a mixture of two soluble solids (by making up a solution of known total solid content).

Let us now consider the application of the instrument to the analysis of a simple solution—of a single salt dissolved in water; the procedure of course is substantially identical in all cases. The interferometer may be used for the analyses of solutions in two ways: (1) as a direct reading instrument, (2) as a zero instrument. In either method the zero reading of the instrument is first obtained by bringing the fringes to coincidence when water (or the same solution) is placed in each compartment of the chamber; these “zero” readings, which, however, vary only very slightly from one day to another, are in all cases subtracted from the final readings.

In the first method, which is the one generally used heretofore, a series of solutions of the salt, of known concentration, are made up, and compared on the interferometer with samples of the water used in making up the comparison solutions. The readings¹ r are plotted against the

¹ Or preferably the values of the closely related quantity r' (*cf. postea*).

values of the concentration (c); the most convenient way of doing this is to plot r against c/r and to connect the series of points by a smooth curve. The concentration of any solution of this salt can then be determined by observing the reading when it is compared with water (preferably the water from which this solution was made up) and interpolating by means of the curve.

The sensitiveness and range depend on the length of the water chamber, which is supplied in 4 sizes, 5, 10, 20 and 40 mm. in length; in all cases settings can be made to one division on the drum and there are altogether the equivalent of 3,000 divisions. With the 40 mm. chamber one division corresponds to 1.5–3.0 parts substance per million of water for most aqueous solutions; the greatest differences of concentration which can be directly compared are therefore from 0.45–0.9%. An increase of range can be obtained either by using a shorter chamber (with corresponding loss in sensitiveness) or by using throughout as the comparison substance a standard solution of the salt in place of water.

The relative sensitiveness of the usual form of Water Interferometer for various substances in aqueous solution may be seen by referring to Table I. The column headed $\Delta c/\Delta r$ gives the amount of each salt (in parts per million parts of water) corresponding to one scale division when the 40 mm. chamber is used.

TABLE I.

Sensitiveness in parts per million per scale division ($\Delta c/\Delta r$) of the Zeiss Interferometer (with 40 mm. chamber) for various substances in aqueous solution.

| Substance. | $\Delta c/\Delta r$. | Substance. | $\Delta c/\Delta r$. | Substance. | $\Delta c/\Delta r$. |
|---------------------------------------|-----------------------|---|-----------------------|---------------------------------------|-----------------------|
| NaCl..... | 1.9 | K ₂ C ₂ O ₄ | 2.5 | ZnSO ₄ | 1.9 |
| NaBr..... | 2.5 | NH ₄ Cl..... | 1.7 | H ₂ BO ₃ | 4.4 |
| NaI..... | 2.4 | NH ₄ Br..... | 2.3 | CH ₃ OH..... | 17.8 |
| NaNO ₃ | 3.0 | NH ₄ NO ₃ | 2.5 | C ₂ H ₅ OH..... | 5.7 |
| Na ₂ SO ₄ | 2.2 | (NH ₄) ₂ SO ₄ | 2.0 | Glycerine..... | 3.4 |
| KCl..... | 2.5 | MgCl ₂ | 1.3 | Mannite..... | 2.4 |
| KBr..... | 2.8 | MgSO ₄ | 1.7 | Cane sugar..... | 2.3 |
| KI..... | 2.6 | CaCl ₂ | 1.4 | Levulose..... | 2.8 |
| KNO ₃ | 3.6 | SrCl ₂ | 1.9 | Dextrine..... | 3.0 |
| K ₂ SO ₄ | 2.7 | BaCl ₂ | 2.3 | | |

In the second method the solution of unknown concentration is compared directly with two known solutions, one preferably of slightly higher, the other of slightly lower concentration, which should differ from one another by not more than 200 scale-divisions; from these two readings its concentration is then easily interpolated. This method requires the use of but a small portion of the scale of the interferometer, and presupposes an approximate knowledge of the concentration of the solution. Of the two methods the latter, while in general somewhat more laborious, is applicable to solutions of any concentration and is not subject to the

source of error noted below. The former method (1), on the other hand, while inherently more convenient and more rapid, is subject to a disadvantage connected with a phenomenon already noted by Marc¹ (in the case of colloidal solutions only)—the alteration and apparent shift of the white central band. This phenomenon, which is of general occurrence with compensation interferometers used with white light,² is an insidious source of error, which must be guarded against; its cause and the means of predicting in advance the exact amount of this shift will now be taken up.

Alteration in Character of the Comparison Band; its Apparent Shift.—

In the central or zero position the interference pattern, as seen in the field of the eye-piece, consists of three bright bands, a central white band separated on either side by a narrow black band from the parti-colored adjacent band, each of which is blue on the side towards the center of the field. Now if, by movement of the compensator, the left-hand bright band is brought to the center, it is seen to be not pure white but edged with blue on the right and red on the left, while the neighboring band to the left will be strongly colored on both edges; thus in this case there is no uncertainty as to which is the proper band on which to make the setting. Moreover, if the water in compartment C_1 be replaced by a very dilute solution, the original central achromatic band can (by turning the drum) be brought back into the field of view and distinguished without ambiguity. But in general the situation is somewhat different.

We may best understand what happens by supposing that in some way the concentration of a solution in C_1 is increased slowly and continuously from zero onwards, and that at the same time the original achromatic band is kept central by appropriate movement of the compensator. We would then, in most cases, observe that the original achromatic band gradually becomes colored at the edges, while the adjacent bands to right and left become, respectively, more and less strongly colored; with further increase of concentration the central band becomes identical in appearance with the band on the left, and, at length, the latter is achromatic while the central band is now parti-colored just as the right-hand band was originally. The comparison band has thus *apparently* shifted one band to the left; with further increase of concentration the same sequence of events occurs, and the apparently correct comparison band is shifted one additional band to the left for a certain concentration difference, this difference for KCl being (on our instrument) about 0.07% (280 divi-

Now, since in making readings on a series of solutions of a substance, *Proc. Roy. Soc. Lond., Chem. Zig.*, 36, 539 (1912).

Use of monochromatic light would obviate this difficulty, but on the other hand it necessitates special means to enable one to identify the original central band. The magnitude of this interval varies from one salt to another, being for instance much smaller for KNO_3 than for KCl; cf. *postea*.

stance we ought obviously to make the final setting always upon the same band, we shall err if the setting is made each time upon the most nearly achromatic band; and there will be one discontinuity for each such "concentration interval."

The explanation of this wandering of the original achromatic band is found in the relative optical dispersion of solution and water, on the one hand, and of glass (of the compensator plates $P_1 P_2$) and air, on the other hand. To obtain a quantitative expression for the magnitude of this effect it is first to be noted that in the type of instrument under consideration the lengthening of the optical path due to replacement of water by solution is compensated by the shortening of the *same* path by decreasing the effective thickness of an interposed glass plate. For the refractive indices of solution, water and glass we write n_1 , n_2 , and n , respectively, and put

$$\nu = n_1 - n_2$$

with appropriate subscripts attached to ν to denote the wave length to which it refers. The dispersive power (β') of the solution with respect to water¹ is defined by the relation

$$\beta' = (\nu_F - \nu_C)/\nu_D$$

and similarly,

$$\beta'' = \frac{n_F - n_C}{n_D - 1}$$

Now it can readily be shown² that with an interferometer of the type under discussion the position of the most nearly achromatic band will, as the concentration of the solution increases, shift one fringe to the left for a certain number r_1 of divisions on the drum, where

$$r_1 = 0.320 r_f / (\beta' - q\beta'') \quad (\text{III})$$

r_f being the number of divisions corresponding to one fringe in white light³ and q a constant depending on the refractive index of the compensator plate, and its initial inclination.⁴

Accordingly, the exact amount of the wandering of the achromatic band for any solution may be predicted in advance, and this source of

¹ It is to be noted that this quantity β' is not the same as the difference in relative dispersion of solution and water, i. e.,

$$\frac{n_{1F} - n_{1C}}{n_{1D} - 1} - \frac{n_{2F} - n_{2C}}{n_{2D} - 1} \text{ is not equal to } \frac{\nu_F - \nu_C}{\nu_D}$$

β'' on the other hand is the ordinary relative dispersion of the glass.

² See L. H. Adams, *J. Wash. Acad.*, 5, 276 (1915).

³ Or more specifically the light of the tungsten lamp which is ordinarily used as the light-source.

⁴ For the ordinary case of an initial inclination of about 45° and refractive index n ,

$$q = \frac{2n(n-1)}{(2n^2-1)^{1/2} - (2n^2-1)}$$

error thus guarded against, if the appropriate values of β' and β'' are known. The value of β'' for various kinds of glass may be found in tables of constants;¹ thus for the (crown) glass, of which the compensator plates in our instrument are made, $\beta'' = 0.015$, $n = 1.514$, and therefore $q = 0.48$.

β' has been measured for various salts in aqueous solution;² for KCl it is about 0.032. Consequently for a series of solutions of KCl (taking $r_f = 22$)³ $r_1 = 0.320 \times 22/0.025 = 280$ divisions; therefore, at a concentration corresponding to 140 scale divisions the originally white central band will have become identical in appearance with the left-hand band and at 280 divisions the original left-hand band will have become the achromatic one. This difficulty could be entirely obviated by using compensator plates of such glass that $q\beta' = \beta''$ for the solutions (or mixtures) under investigation. But, unfortunately, this can be done only to a limited extent, for high dispersion in glasses is accompanied by high refractive index, so that even in the extreme case of heaviest flint glass, $\beta'' = 0.051$, $n = 1.963$, $q = 0.35$, and therefore $q\beta''$ is only 0.018, while the corresponding quantity β' may be as high as 0.045 for solutions such as the nitrates and even higher for other salts such as the bromides and iodides. But, at any rate, it would be an improvement to substitute compensator plates of heavier optical glass for the usual crown glass ones. Thus compensator plates of the glass mentioned above (Jena optical glass No. S 57) would match all sulfate solutions (β' about 0.016) very well and for use with all other solutions would be at least as suitable as crown glass plates. But in general this difficulty of the wandering of the achromatic band can only be circumvented by recourse to one of two methods of procedure: (1) the employment of the "zero method" described above, which is in general the more satisfactory mode of operation, for in that case dispersion differences are of little consequence and in most cases will not lead to error, especially if the maximum reading in the scale is never greater than 100 or 200 divisions; or (2) a careful preliminary determination of the "concentration intervals," using as a guide Equation III above and the following Table II which summarizes the available mean values of β' for salts and other substances in aqueous solution. But it may be worth while to make this series of preliminary observations and so be enabled to use the direct method in the not infrequent case when a large number of similar solutions have to be analyzed; it is for this reason that this question of the shifting of the achromatic band has been discussed here at some length.

¹ Thus Landolt-Börnstein-Roth (p. 980) gives "reciprocal relative dispersion" $1/\beta'$.

² W. Hallwachs, *Ann. Physik*, 47, 381 (1891); A. H. Borgesius, *Ann. Physik*, 54, 221 (1895); D. Dijken, *Z. physik. Chem.*, 24, 81 (1897).

³ On our instrument r_f for white light varies from 22 at the lower end of the scale to about 28 at the upper end.

TABLE II.

Mean Values of β' ($= (\nu_F - \nu_C)/\nu_D$) for Various Substances in Aqueous Solution.

| Substance. | β' . | Substance. | β' . | Substance. | β' . |
|-------------------------|------------|---|------------|---|------------|
| LiCl..... | 0.037 | NaBr..... | 0.047 | Na ₂ SO ₄ | 0.016 |
| NaCl..... | 0.036 | KBr..... | 0.045 | K ₂ SO ₄ | 0.015 |
| KCl..... | 0.032 | LiNO ₃ | 0.048 | MgSO ₄ | 0.014 |
| MgCl ₂ | 0.032 | NaNO ₃ | 0.043 | ZnSO ₄ | 0.015 |
| ZnCl ₂ | 0.031 | KNO ₃ | 0.042 | (NH ₄) ₂ SO ₄ | 0.016 |
| BaCl ₂ | 0.028 | Mg(NO ₃) ₂ | 0.038 | H ₂ SO ₄ | 0.022 |
| HCl..... | 0.045 | Zn(NO ₃) ₂ | 0.035 | CH ₃ COOH..... | 0.021 |
| NH ₄ Cl..... | 0.035 | NH ₄ NO ₃ | 0.043 | Cane sugar..... | 0.012 |
| LiBr..... | 0.049 | Li ₂ SO ₄ | 0.017 | | |

Inspection of this table shows that there is a wide range in the values of β' for different substances in aqueous solution; however, the substances may be divided into several groups, in each of which β' is nearly constant. Thus for all of the sulfates β' is not far from 0.016; for the chlorides β' is not far from 0.035, for the bromides 0.047 and for the nitrates about 0.040. The nonelectrolyte, cane sugar (and probably also mannite) is exceptionally low.

Interpretation of the Interferometer Readings in Terms of Refractive Index.—Although the interferometer reading is a measure of a difference in refractive index, a knowledge of refractive indices *per se* is not essential for the analysis of solutions or mixtures, since the readings on an arbitrary scale are converted directly into concentrations by means of a previously determined calibration curve or table. Nevertheless, it is of interest to note the exact connection between the reading r of the instrument and the refractive index differences ν of the mixtures in question. Owing to the manner in which the micrometer screw moves the inclined compensator plate, the readings r on the drum are not quite directly proportional to ν , but by means of a small and easily applied correction they may be made so. It can readily be shown¹ that the change in optical path p caused by the rotation through an angle θ , (reckoned from the initial position at 45° to the light rays), of a plane-parallel plate of thickness h and refractive index n is found by the relation

$$p = \sqrt{2}h(\sqrt{H} - 1 - \sqrt{H} + \sin 2\theta + \cos \theta + \sin \theta)$$

where $H = 2n^2 - 1$. Furthermore, if R is the distance (in mm.) through which the micrometer screw moves and a the constant perpendicular distance from the center of rotation to the line of motion of the screw, then

$$\sin \theta = R/\sqrt{R^2 + a^2}$$

and

$$\cos \theta = a/\sqrt{R^2 + a^2}.$$

Substituting these values in the above expression we have, with sufficient approximation,

¹ See L. H. Adams, *J. Wash. Acad. Sci.*, 5, 267-9 (1915).

$$\frac{p}{\sqrt{2h}} = \frac{R}{a} \left(1 - \frac{1}{\sqrt{H}}\right) - \frac{R^2}{2a^2} \left(1 - \frac{1}{H^{1.5}}\right). \quad (\text{IVa})$$

Let R' be a quantity such that

$$\frac{p}{\sqrt{2h}} = \frac{R'}{a} \left(1 - \frac{1}{\sqrt{H}}\right)$$

then

$$R' = R - \frac{R^2}{2a} \left(\frac{1 - 1/H^{1.5}}{1 - 1/\sqrt{H}} \right). \quad (\text{IVb})$$

Now in our instrument $r \pm 200 R$, $a = 110$ mm., $n = 1.51$. Making these substitutions we obtain finally the relation (for our instrument)

$$r' = r - 0.000041 r^2. \quad (\text{IV})$$

R' (and hence also r') is a number proportional to the decrease in optical path of the compensator plate, and therefore is strictly proportional to the quantity ν .

Although not essential, it is advantageous to use r' rather than r in all work with the interferometer; because, as the concentration c varies, the variation of the quotient c/r' is more regular than that of c/r . In the case of practically all substances in aqueous solution, c/ν , and hence c/r' , increases slowly with increasing concentration; c/r on the other hand usually decreases rather rapidly, while in using the zero method one may obtain values of c/r (the concentration gradient) which increase and decrease in a very irregular way, depending on the magnitude of c and of r . The data of Table III on mannite solutions (for which I

TABLE III.

| Conc. parts per million. | c . (Av.) | Δc . | r . | $\Delta c/r$. | r' . | c/r' . |
|-----------------------------|----------------|--------------|-------|----------------|--------|----------|
| 504 0 | 252 | 504 | 217 | 2.32 | 215 | 2.34 |
| 1024 0 | 512 | 1024 | 447 | 2.29 | 438 | 2.34 |
| 4063 2541 | 3302 | 1522 | 669 | 2.27 | 650.5 | 2.34 |
| 4563 4063 | 4313 | 500 | 214 | 2.34 | 212 | 2.36 |
| 14154 13904 | 14029 | 250 | 105 | 2.38 | 104.5 | 2.39 |

am indebted to Mr. R. E. Hall) illustrate this point. Inspection of this table, which is self-explanatory, shows the much greater regularity of the concentration gradient obtained by converting the readings r into the "corrected" readings r' according to Equation IV. This procedure not only makes for greater convenience in plotting calibration curves and interpolating from them, but, in addition, it renders the detection of errors from various sources much more easy and certain.

As an example of the numerical relation between r' and ν we may take the following case:

A KCl solution containing 357 parts per million of water gives in the 40 mm. chamber of our instrument a reading $r = 150$, which by Equation IV corresponds to $r' = 149$. The retardation N in wave-lengths, is then $N = r'/r_f = 149/22.0 = 6.78$, and by Equation II, $\nu = N\lambda/l$. Here l is twice the length of the chamber or 80 mm. Hence, taking $\lambda = 0.00058$ mm. we have the difference in refractive index between solution and water, $\nu = 0.0000497$ at 22° . This result may be compared with the results of Dijken² and Borgesi³ for KCl solutions. By interpolation from their results ν_D at 22° for the same KCl concentration is 0.0000505 (Dijken), 0.000478 (Borgesi³).

Concluding Remarks.—A few hints with regard to methods which have proved useful in actual working with the instrument may be worth mentioning. Changing of solutions is effected by means of a pipet (preferably provided with a rubber syringe bulb), over the tip of which is slid a small piece of rubber tubing in order to obviate damage to the water chamber. It is advisable to rinse two or three times; filter paper can be used to absorb the few drops remaining in the chamber each time, except in the final rinsing. One must wait until the temperature of the solutions is uniform, since otherwise the bands are distorted. Several independent settings of the drum should be made on each sample of solution, and it is advisable for the highest accuracy to take readings on more than one sample of each solution.

It has already been mentioned that one advantage of the interferometer is its insensitiveness to temperature changes as compared with ordinary refractometers. The temperature coefficient is not absolutely *nil*, however; for example, in the case of KCl solutions it is about -0.2% per degree (at 20 – 25°) and for KNO_3 solutions about -0.5% per degree; that is, if in reading one KCl solution against another we find $r = 200$ at 25° , the corresponding reading at 20° would be 202. It is evident that for small temperature fluctuations and with small readings such as are obtained when using the "zero" method, the temperature effect may be neglected; but if greater accuracy is desired the temperature coefficients may easily be determined and the necessary small corrections applied.

A number of possible applications of the interferometer to chemical work has already been suggested at various times. The instrument was originally designed for the analysis of sea-water and has been successfully used for that purpose, while Marc has employed it for the analysis of colloidal solutions. Another purpose for which the interferometer would be especially suitable is the standardization of solutions for volumetric analysis; other uses will readily suggest themselves. One such use only

¹ N , and hence ν , may be calculated without reference to r' by using formula IVa and knowing h and n for the compensator plate.

² D. Dijken, *Z. physik. Chem.*, 24, 96 (1897).

³ A. H. Borgesi³, *Ann. Physik*, 54, 233 (1895).

will be mentioned; namely, that mixtures of sodium and potassium salts may be rapidly analyzed with an accuracy equaling or even exceeding that of the most careful gravimetric analyses. For instance, suppose we wish to determine the amounts of soda and potash in a mixture of their sulfates, which need not weigh more than 50 mg. altogether. We dissolve this mixture in exactly 200 times its weight of water and compare it on the interferometer with a standard solution containing pure, dry K_2SO_4 dissolved in 200 times its weight of water; the reading will range from 430 to 0 as the composition of the mixture ranges from pure $NaSO_4$ to pure K_2SO_4 . In this way any mixture can, with the aid of a calibration curve previously determined once for all, be analyzed in a few minutes with an accuracy of 0.1 mg. of either constituent (on a 50 mg. sample).

Summary.

The foregoing pages present a brief description of the principle and mode of operation of the interferometer, a form of instrument which enables one to determine the single varying constituent in a mixture or solution, with ease, rapidity, and very great accuracy. The only important source of error arises from differences in optical dispersion; it can readily be obviated by use of the methods discussed in the text.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF JOHNS HOPKINS UNIVERSITY.]

THE VISCOSITIES OF BINARY MIXTURES OF THE ASSOCIATED LIQUIDS, WATER, FORMIC ACID AND ACETIC ACID.¹

By P. B. DAVIS AND HARRY C. JONES.

Received March 16, 1915.

Jones and Murray² showed in 1903 that when two associated liquids are mixed, each diminishes the association of the other. They determined the molecular weight of water in formic acid on the one hand, and in acetic acid on the other. Also the molecular weight of formic acid in water, and in acetic acid, and finally the molecular weight of acetic acid in water and in formic acid.

They found that the molecular weight of water in formic acid varied from 19.7 at dilution 0.93 *N* to 21.9 at 6.18 *N*, showing that the formic acid diminished slightly the association of the water.

The molecular weight of water in acetic acid varied from 21.7 at 0.64 *N* to 38.8 at 12.65 *N*. This showed that the acetic acid diminished greatly the association of the water.

¹ This work was done in connection with an investigation which is being carried out with the aid of a Grant from the Carnegie Institution of Washington, to H. C. Jones.

² *Am. Chem. J.*, 30, 193 (1903).

The molecular weight of acetic acid in water varied from 55.4 at 0.17 *N* to 72.1 at 7.06 *N*, showing that water diminished very appreciably the association of acetic acid.

The molecular weight of acetic acid in formic acid varied from 61.9 at 0.18 *N* to 83.8 at 9.17 *N*. The association of the acetic acid was thus diminished considerably by the formic acid.

The molecular weight of formic acid in water varied from 45.2 at 0.38 *N* to 51.0 at 6.16 *N*, showing that water had very little effect on the association of the formic acid; and, finally, the molecular weight of formic acid in acetic acid varied from 50.4 at 0.82 *N* to 65.7 at 8.26 *N*.

If we take into account the dissociating action of the water on the formic and acetic acids, we are justified in concluding that water and formic acid affect each other's association very little; acetic acid and formic acid affect each other's association considerably, while both water and acetic acid have a marked effect each on the association of the other.

These facts were used by Jones and Veazey¹ to explain the increase in viscosity which takes place when water and alcohol are mixed. These are both strongly associated solvents, and each, therefore, very probably diminishes appreciably the association of the other. From a smaller number of larger molecules of each solvent, we have a larger number of smaller molecules of each solvent produced. The surfaces of the molecules present are therefore increased, and, consequently, the friction of these molecules as they move over one another. Viscosity is a function of the surface friction of the molecules.

In the same manner Jones and Veazey² were able to explain why it is that salts of potassium, rubidium and caesium lower the viscosity of water and other solvents³ in which they are dissolved. The large atomic volumes of these cations when mixed with the molecules of water, diminish the frictional surfaces which come in contact, and, consequently diminish the viscosity.

Having found the above action of water, formic acid and acetic acid, each on the association of the other, the question arose, what would be the effect of each on the viscosity of the other? If the above explanations offered by Jones and Veazey were correct, then two liquids, like water and acetic acid, which diminished each others association, ought to increase the viscosity of one another—the viscosity of the mixture should be greater than that of either pure liquid separately.

The viscosities of binary mixtures of the above-named three liquids were measured at 15° and 25°. Water was regarded as the solvent for

¹ *Z. physik. Chem.*, 61, 641; 62, 44 (1908); Carnegie Institution of Washington, Publication No. 80, 170 (1907).

² *Loc. cit.*

³ Jones and Davis, *Z. physik. Chem.*, 81, 68 (1912); Carnegie Institution of Washington, Publication No. 180, 179 (1913).

formic acid and acetic acid, and solutions of these acids in water were prepared containing by volume 10, 20, 30, 40, 50, 60, 70, 80, 90%. The acids themselves contained somewhat less than 1% of water. The viscosity and the fluidity (reciprocal of viscosity) data are given in the following tables:

TABLE I.—VISCOSITIES AND FLUIDITIES OF FORMIC ACID IN WATER AT 15° AND 25°.

| Per cent. HCOOH. | η 15°. | ϕ 15°. | η 25°. | ϕ 25°. |
|--------------------|-------------|-------------|-------------|-------------|
| (H ₂ O) | 0.01134 | 88.18 | 0.00891 | 112.23 |
| 10 | 0.01215 | 82.31 | 0.00932 | 107.3 |
| 20 | 0.01282 | 78.00 | 0.01014 | 98.62 |
| 30 | 0.01339 | 74.68 | 0.01072 | 93.28 |
| 40 | 0.01408 | 71.02 | 0.01135 | 88.11 |
| 50 | 0.01469 | 68.07 | 0.01202 | 83.20 |
| 60 | 0.01591 | 62.85 | 0.01287 | 77.70 |
| 70 | 0.01693 | 59.07 | 0.01371 | 72.94 |
| 80 | 0.01803 | 55.46 | 0.01452 | 68.87 |
| 90 | 0.01914 | 52.25 | 0.01546 | 64.68 |
| (HCOOH) | 0.01963 | 50.94 | 0.01571 | 63.65 |

TABLE II.—VISCOSITIES AND FLUIDITIES OF ACETIC ACID IN WATER AT 15° AND 25°.

| Per cent. CH ₃ COOH. | η 15°. | ϕ 15°. | η 25°. | ϕ 25°. |
|---------------------------------|-------------|-------------|-------------|-------------|
| (H ₂ O) ¹ | 0.01134 | 88.18 | 0.00891 | 112.23 |
| 10 | 0.01368 | 73.10 | 0.01059 | 94.43 |
| 20 | 0.01626 | 61.50 | 0.01244 | 80.39 |
| 30 | 0.01897 | 52.72 | 0.01446 | 69.16 |
| 40 | 0.02143 | 46.66 | 0.01624 | 61.58 |
| 50 | 0.02416 | 41.39 | 0.01818 | 55.01 |
| 60 | 0.02682 | 37.29 | 0.02015 | 49.63 |
| 70 | 0.02935 | 34.07 | 0.02219 | 45.07 |
| 80 | 0.03068 | 32.60 | 0.02318 | 43.14 |
| 85 | 0.03033 | 32.90 | 0.02292 | 43.63 |
| 90 | 0.02786 | 35.89 | 0.02115 | 47.28 |
| 95 | 0.02243 | 44.58 | 0.01775 | 56.34 |
| CH ₃ COOH | 0.01410 | 70.92 | 0.01174 | 85.18 |

TABLE III.—VISCOSITIES AND FLUIDITIES OF FORMIC ACID IN ACETIC ACID AT 15° AND 25°.

| Percent. HCOOH. | η 15°. | ϕ 15°. | η 25°. | ϕ 25°. |
|------------------------|-------------|-------------|-------------|-------------|
| (CH ₃ COOH) | 0.01410 | 70.92 | 0.01174 | 85.18 |
| 10 | 0.01558 | 64.19 | 0.01286 | 77.76 |
| 20 | 0.01701 | 58.79 | 0.01391 | 71.89 |
| 30 | 0.01792 | 55.80 | 0.01463 | 68.35 |
| 40 | 0.01883 | 53.11 | 0.01506 | 66.40 |
| 50 | 0.01942 | 51.49 | 0.01564 | 63.94 |
| 60 | 0.01984 | 50.40 | 0.01587 | 63.01 |
| 70 | 0.02012 | 49.70 | 0.01607 | 62.23 |
| 80 | 0.02002 | 49.95 | 0.01607 | 62.23 |
| 90 | 0.01967 | 50.84 | 0.01582 | 63.21 |
| (HCOOH) | 0.01963 | 50.94 | 0.01571 | 63.65 |

¹ Values for water taken from Thorpe & Roger, *Phil. Trans.*, 185A, 449 (1894).

The viscosity data at 15° are plotted in curves, Fig. 1; and the viscosity data at 25° in curves, Fig. 2. The viscosities of acetic acid in water pass through a well-defined maximum, which, before we carried out a single measurement of the viscosities of mixtures of these two solvents,¹ we predicted, would be the case from the molecular-weight determinations of this acid in water made by Jones and Murray.

The viscosities of formic acid in acetic acid pass through a slight maximum, as would be expected from the effect of each of these solvents on the molecular weight of the other.

The viscosities of mixtures of water and formic acid, on the other hand, fall almost on a straight line. This again is just what would be expected, from the fact that neither solvent alters appreciably the molecular weight of the other.

These results are, then, all in keeping with

¹ Since completing our work, we find that a few measurements of the viscosities of mixtures of acetic acid in water had been made by Dunstan and Thole, *J. Chem. Soc.*, 85, 825 (1904); 95, 1560 (1909).

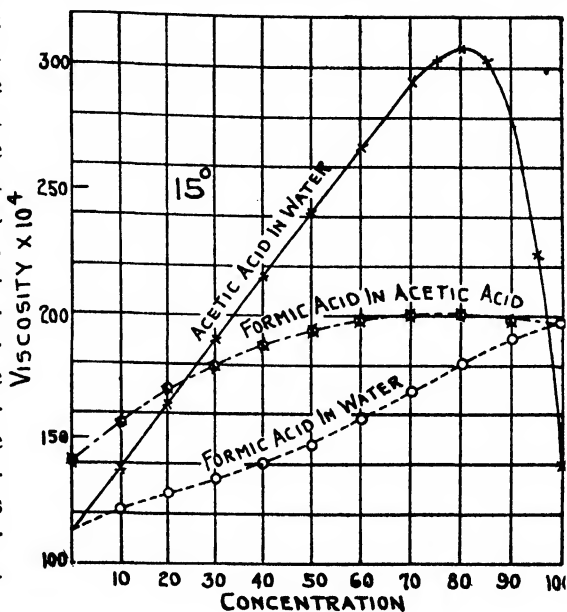


Fig. 1.

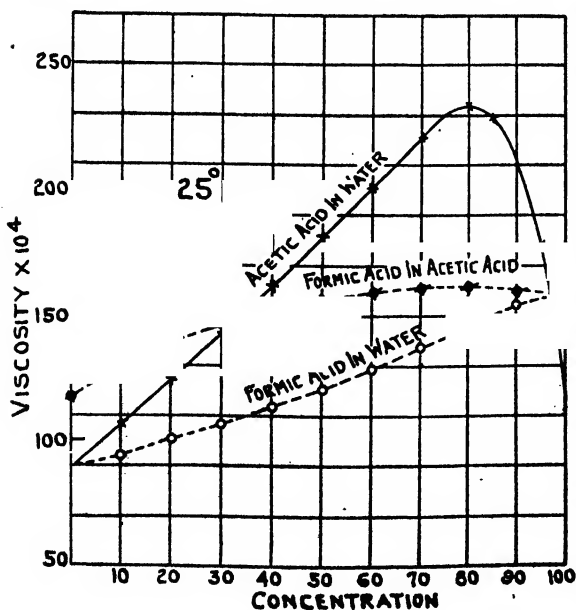


Fig. 2.

the suggestion made by Jones and Veazey, that the increase in viscosity which results when associated liquids which diminish each other's association are mixed, is due to the *larger number of smaller parts* that are present.

These results are also in perfect accord with their suggestion as to the cause of the diminution in the viscosity of water, produced by salts whose cations have very large ionic volumes, such as salts of potassium, rubidium and caesium.

JOHNS HOPKINS UNIVERSITY.

NOTES.

Some New Forms of Apparatus: I. A Substitute for the Twin-bulb Trap in Toluene-Mercury Thermoregulators.—Toluene, on account of its high coefficient of expansion, is to be preferred to all other liquids for use in thermoregulators. Since, however, it is practically a nonconductor and quite volatile, it is ordinarily used with mercury for the contact in all electrically operated thermostats.

In order to use these two liquids together, the common form of apparatus hitherto employed has been the twin-bulb device, which, however, has the following disadvantages:

1. It is very fragile and can only be made by an expert glass-blower.
2. When the mercury level in the capillary has been once adjusted for any given temperature and the toluene reservoir sealed, the regulator is practically useless for any higher temperatures without opening the reservoir and removing the excess of toluene in order to preserve the equilibrium in the two bulbs.
3. It is difficult to prevent the toluene from finally creeping around between the mercury and the glass walls into the capillary and fouling the contact surface of the mercury, since the same continuous tube contains both the toluene and mercury.

To overcome these difficulties as far as possible the apparatus illustrated in Fig. 1 has been devised. This consists of a bulb (a) attached at the bottom by the tube (b) to the toluene reservoir which may be of any desired form. Exactly opposite to (b) is a corresponding tube (c), which carries the capillary and sealed-in platinum contact.

The interior construction of (a) is as shown in the figure. The small tubes (e) and (f) are prolongations of (c) and (b), respectively, having a length nearly equal to

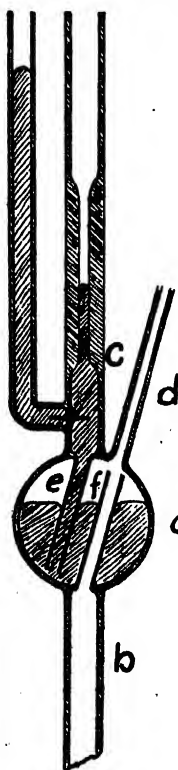


Fig. 1.

the diameter of the bulb. These tubes are inclined at an angle of about 30° from the perpendicular. The short side tube (*d*) is used in filling the regulator and is in exact alignment with (*f*).

To prepare the regulator for use, mercury is poured in through the capillary until the bulb (*a*) is from one-half to three-fourths filled. A tube drawn out to a small diameter is then inserted through (*d*) and (*f*) into (*b*), and toluene allowed to run in until the reservoir is filled and also the space in (*a*) above the mercury. The tube (*d*) is then sealed, and by adding or withdrawing mercury from the capillary the contact level may be adjusted for any desired temperature.

By this method a toluene-mercury regulator is constructed with a range of 50° or more, all adjustments being made through the capillary which should be of from 1.5 to 2 mm. bore, according to the capacity of the toluene reservoir.

All danger of the toluene creeping into the capillary is removed since the tubes (*e*) and (*f*) terminate in the same liquid which is contained in them.

This trap is compact, not easily broken and is comparatively simple to construct. In addition to this it lies within the plane of the reservoir and contact tubes.

P. B. DAVIS.

II. A New Form of Pycnometer for Liquids.—The authors have recently had occasion to carry out a large number of density determinations with various liquids. For this purpose a modified form of the Sprengel pycnometer, as described by Jones and Bingham¹ and Jones and Veazey,² was first adopted, but was found to have the following disadvantages:

1. In instruments of large capacity (10 to 20 cc.) the long capillary side-arm adds greatly to the weight and hence impairs the accuracy of the pycnometer.

2. The fragility of the older form makes rapid handling practically impossible.

3. The instrument is difficult to dry and polish before weighing.

To remove these defects the form shown in Fig. 2 was devised, and has been found to be more convenient and accurate than the old form.

In the figure the symbols have the following significance:

(*a*) A reservoir of thin-walled glass tubing which may be of any desired capacity; those in use in this laboratory holding, respectively, about 6, 10 and 20 cc.

(*b*) Tapering tube of thin glass reaching almost to the bottom of (*a*), and having a bore at the open end equal to or slightly greater than that of

¹ *Amer. Chem. J.*, 34, 48 (1905).

² *Z. phys. Chem.*, 61, 641 (1908).

the capillary (0.5–0.75 mm.). This tube is of use in drying and filling the instrument.

(c) Outlet tube sealed on to the end of (b). This is drawn out slightly at the end and is bent at an angle of 60° close to the reservoir.

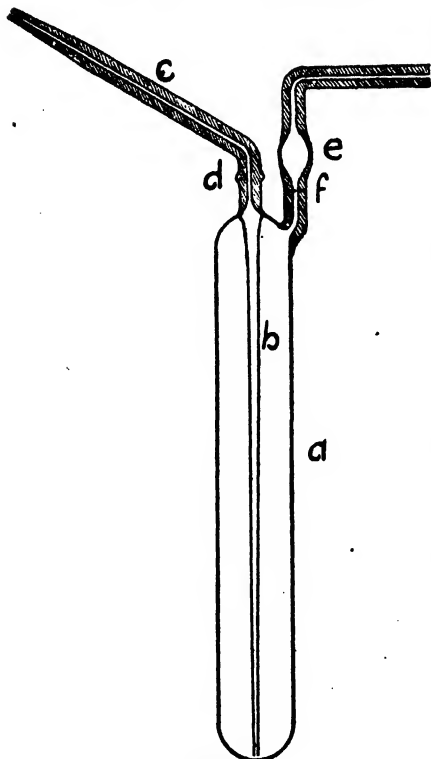


Fig. 2.

(d) Slight enlargement in (c) which holds in position the wire used to suspend the pycnometer on the balance.

(e) Expansion bulb of sufficient size to accommodate the increased volume of any liquid when warmed 10° . If the instruments are used only at 25° this bulb need be only very small.

(f) Fine line etched around the capillary at the lower limit of the taper in the bulb (e).

In adjusting the instrument when filled, a rubber tube is attached to the horizontal capillary above (e), and the liquid blown out gently until the level in (e) just reaches the mark (f). The excess of liquid is then removed from the end of (c) with filter paper. On removing the pressure, the level of the liquid in (c) falls until it comes to rest near

the bend in the capillary, thereby lessening the danger from evaporation or accidental spilling after adjustment.

The advantages of this form of pycnometer can readily be seen, e. g., the projecting arms are both short and hence not easily broken. Also the net weight has been materially lessened, since the amount of necessary capillary has been reduced to a minimum. The instrument is also much easier to clean and dry before weighing than the older form.

This pycnometer may be provided with ground-on caps when used with alcohol or other volatile liquids, to prevent possible evaporation.

CHEMICAL LABORATORY, JOHNS HOPKINS UNIVERSITY. P. B. DAVIS AND L. S. PRATT.

CORRECTIONS.

Professor James M. Bell has kindly called my attention to an article by Bell and Taber,¹ which was overlooked by me in my article on the

¹ *J. Phys. Chem.*, 12, 171 (1908).

determination of hydrates.¹ In this work, the authors determined, as we did, the solubility of copper sulfate in sulfuric acid solutions at 25° and Professor Bell has now recalculated the solubility results to a common basis and finds our results confirm his earlier ones. The composition of the hydrates in equilibrium with the solutions was determined by Bell and Taber by the method of residues and graphical extrapolation. We obtained the residues free from mother liquor by treatment with alcohol, depending on the composition of the solutions in a series of determinations for information as to whether the residues thus obtained were pure hydrates or mixtures of two. Both investigations show the presence of the same hydrates. Bell and Taber also calculated the approximate vapor pressures of the hydrates from the vapor pressures of the solutions, a point which we briefly considered without knowing of their work.

H. W. FOOTE.

The Stannic-Stannous Potential.—Mr. H. W. Richter, at present collaborating with one of us, has kindly called our attention to an error in our paper entitled "The Measurement of Oxidation Potentials at Mercury Electrodes. I. The Stannic-Stannous Potential," *THIS JOURNAL*, 36, 2035 (1914). Owing to neglect of the temperature coefficient of the normal calomel electrode, its electromotive force at 25° was assumed as 0.560 instead of 0.564 volt. Therefore, 0.004 volt must be added to each of the single potentials recorded, and the value of the stannic-stannous potential at 25° becomes

$$\pi = 0.430 + 0.030 \log \frac{\text{Sn}^{\text{IV}}}{\text{Sn}^{\text{II}}} - 0.011 \times \text{conc. HCl.}$$

GEORGE SHANNON FORBES AND EDWARD PAYSON BARTLETT.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

THE ORCINOLPHTHALEINS, THE ORCINOLTETRACHLOROPHTHALEINS, AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND E. R. ALLEN.

Received March 9, 1915.

Historical.

Orcinolpthalein was first made and studied by Emil Fischer,² working under the direction of A. von Baeyer at Strassburg, and the results published as his inaugural dissertation in 1874. He obtained small amounts of this phthalein by heating orcinol and phthalic anhydride to 210–220°. Much better results were obtained by heating freshly fused anhydride, distilled orcinol and concentrated sulfuric acid for two hours to 135°.

¹ *THIS JOURNAL*, 37, 288 (1915).

² *Ann. (Liebig)*, 183, 63 (1876).

Final purification was effected by crystallization from acetone or from glacial acetic acid. The analyses of the product dried at 180° agreed with the formula $C_{22}H_{16}O_6$, and a structure analogous to that held for fluorescein at that time was proposed for it.

Dilute alkalis and ammonia dissolve it readily with an intensely dark red color. The solutions of the pure substance show no fluorescence, those of the crude product only a faint greenish fluorescence.

The phthalein showed no melting point, decomposing at about 230° . By boiling the phthalein with acetic anhydride he obtained a colorless product, insoluble in alkalis, which gave results on analysis for the diacetyl derivative. It is completely analogous to diacetyl fluorescein, and melts at $219-220^{\circ}$.

According to Fischer the behavior of orcinolphthalein toward glacial acetic acid is peculiar; for, while with care it can be crystallized in short, perfectly colorless prisms, if the solution be heated for some time the crystals suddenly turn yellowish red, and even by repeated crystallization they cannot again be obtained colorless. This colored compound dissolves in alkalis with the same color as the pure phthalein, but is precipitated unchanged by acetic acid. Before the reason for this phenomenon was understood the purification of the phthalein was rendered unusually difficult, since at one time colorless crystals were obtained from acetic acid, while at another they were red. Further investigation led Fischer to conclude that this conversion was caused by the acetic acid itself. By heating the phthalein with acetic acid in a sealed tube to 150° he obtained a compound, which, on analysis gave results approximating those required for a monoacetyl derivative, *i. e.*, $C_{22}H_{16}O_6(C_2H_3O)$.

Calculated: C, 71.64; H, 4.47; found: C, 72.13; H, 4.46.

The high carbon content found he attributes to a slight admixture with the phthalein (see p. 1205).

As an example of the dark red compounds which orcinolphthalein forms with mineral acids Fischer isolated and analyzed the hydrochloride. Even in the cold hydrochloric acid colors the white phthalein red, but for complete conversion an excess of hydrochloric acid is added to an alcoholic solution of the phthalein, which becomes colored dark red. On evaporating the alcohol, the compound separates in dark red flocks. These were dried in a vacuum over sulfuric acid. They then analyzed in close agreement with the formula $C_{22}H_{16}O_6.HCl$.

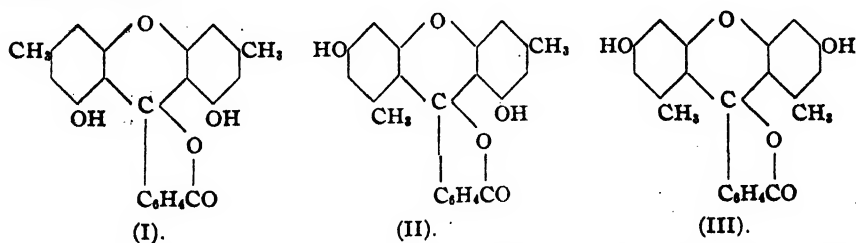
On the addition of bromine in excess to the boiling glacial acetic acid solution of the pure phthalein, the tetrabrom substitution product was obtained. Its solution in alkalis has an almost black color, which on dilution becomes dark brown, and shows a peculiar blackish green fluorescence (see p. 1207). In regard to the positions occupied by the bromine atoms Fischer points out that they are probably equally distributed

between the two orcinol residues, since each of these contains but two hydrogens in the benzene nucleus.

Baeyer and Fischer point out, in conclusion, that a comparison of fluorescein with orcinolphthalein shows that, in spite of their analogous constitution, they show surprising differences in physical and chemical properties.

Later¹ Richard and Heinrich Meyer took up the study of orcinolphthalein to see if an explanation for this great lack of analogy between orcinolphthalein and fluorescein could be found. The differences were mainly that orcinolphthalein is only formed with condensing agents, and that it dissolves in alkalis with a carmine red color without fluorescence. Orcinolphthalein then resembles more closely in its formation and properties phenolphthalein than fluorescein.

As in the investigation of hydroquinonephthalein² they determined whether the orcinolphthalein contained an anhydride oxygen as firmly bound in a ring as in the case of fluorescein, by benzoylating in alkaline solution, assuming that if the phthalein contained a pyrone ring a dibenzoate would be formed, but, if a less stable anhydride ring were present, during the benzoylating it would be ruptured and a tetrabenzoate would result in consequence of the formation of two new hydroxyl groups. Experiment decided the question in favor of the first assumption. Orcinolphthalein prepared according to the method of Fischer gave a well characterized dibenzoate by the Schotten-Baumann reaction, a direct benzoyl determination proving beyond a doubt that the formula was $C_{22}H_{14}O_6 \cdot (C_7H_5O)_2$. In purifying this dibenzoate, however, R. and H. Meyer obtained two other benzoates, which could be only incompletely separated by means of solvents, one of which, on saponification, gave a cherry-red, the other a green fluorescent solution. This led to the conclusion that in the crude orcinolphthalein a mixture of the three possible structural isomers existed.



This assumption was proved correct by their subsequent work. The third formula belongs undoubtedly to the fluorescent substance, which is a true fluorescein, giving on bromination an eosin, but which formula to

¹ *Ber.*, 29, 2627 (1896).

² *Ibid.*, 28, 2959 (1896).

assign to each of the other two isomers they were unable to decide. To distinguish between the three isomers they designate the product of Emil Fischer,¹ soluble in alkalis with a carmine red color as α , the one soluble in alkalis with a cherry-red color as β , and the one soluble with fluorescence as γ .

They state that as a result of experiments with different condensing agents they found that sulfuric acid, zinc chloride, tin tetrachloride, phosphorus pentoxide, or ferric chloride gave a product consisting chiefly of approximately equal parts of the α - and β -compounds, with only subordinate amounts of the γ -, while if glacial phosphoric acid be used the γ -product was obtained in relatively better yields (see p. 1215).

For separating the isomers they depended on their different behavior towards alkalis. α -Orcinolphthalein is soluble only in caustic alkalis, but not in ammonia or the alkali carbonates; the β -compound dissolves easily in the latter also, but not in a solution of ammonium sesquicarbonate; γ -orcinolphthalein unites even with ammonia gas to form an ammonium salt easily soluble in water.

In the experimental part of their paper the authors state that the best way to obtain the crude product is to follow the directions of Emil Fischer, and add, that if, instead of concentrated sulfuric acid as a condensing agent, phosphorus pentoxide be used a better yield of the γ -isomer is obtained.

The crude fused mass was poured into cold water, and the orange colored precipitate dissolved in sodium hydroxide. The mixture of the three phthaleins was precipitated by dilute sulfuric acid, and washed free from inorganic impurities by means of hot water. The residue was then dried at 120°, finely ground and treated under a bell jar with gaseous ammonia for some hours. By means of water the ammonium salt of the γ -phthalein was dissolved with a brown color and greenish fluorescence. From the residue, dilute ammonium sesquicarbonate (1 : 15) dissolves the remainder of the γ -compound, leaving only the α - and β -phthaleins, and from this mixture cold soda solution removes all the β -compound, leaving almost pure α -phthalein.

They observe that this separation is not absolutely sharp, especially when working with large amounts of material, but it sufficed for the preliminary work, since each compound was further purified as described below.

α -Orcinolphthalein.—Besides the above described method, this isomer was obtained by washing the crude product with aqueous ammonia till the latter was no longer colored cherry-red but bluish red. The residue is almost pure α -phthalein and gives at once colorless crystals from glacial acetic acid. These they considered to be pure if their solution in soda was

¹ Fischer's product was probably a mixture of α - and β -orcinolphthaleins (see pp. 1205, 1206 and 1207).

completely decolorized by shaking with ether or remained only faintly bluish red, not cherry-red. Potassium and sodium hydroxides dissolve the α -phthalein readily with a bluish red color. It dissolves in cold ammonia only slightly, and in soda solution only on warming, and even then with difficulty, with the same color. The solutions in ammonia and soda are decolorized on shaking with ether, whereupon the phthalein goes into the ether. Contrary to expectation, a very dilute potassium hydroxide solution acted in the same way (see p. 1225). In all cases a colorless ether solution resulted which, on evaporation, left the free colorless phthalein, and which gave up the phthalein again when treated with concentrated caustic alkali with the production of a red color. This behavior shows the extremely weak acid nature of the α -phthalein. By mixing an alcoholic solution of the phthalein with alcoholic potassium hydroxide a blue potassium salt separated in clusters of small needles having a bronzy luster (see p. 1208).

The red hydrochloric acid addition product described by E. Fischer was also obtained by R. and H. Meyer, from the *pure* α -phthalein but was not isolated or analyzed by them.

The brown "*monoacetate*," mentioned by Fischer (see p. 1202) as formed by heating his phthalein with glacial acetic acid, was never observed by R. and H. Meyer. Heating the α -phthalein with glacial acetic acid in a sealed tube to 150–180° gave them only colorless crystals of the phthalein. They state that the analyses of E. Fischer, as well as his description of the conduct of his *so called monoacetate*, agree so well with those of the β -phthalein described below that it is very probable the two compounds are identical (see p. 1206).

Tetrabromo- α -orcinolphthalein was prepared by dissolving pure α -phthalein in hot glacial acetic acid, and treating with the calculated amount of bromine. The yellow needles which separated were obtained from hot nitrobenzene as flat, yellow prisms which analyzed in agreement with the formula $C_{22}H_{12}Br_4O_6$. These dissolve in alkalis with a violet color, which on heating becomes stronger and pure blue. On cooling the reddish blue color returns (see p. 1220).

β -Orcinolphthalein.—The β -phthalein is found in the cherry-red solution obtained by extracting the crude material, from which most of the γ -compound had been removed, with soda. From this solution acids precipitate a bright yellow compound, which was purified by dissolving in ammonia, precipitating with sulfuric acid, and washing with water. The residue was dissolved in alcohol and hot water added until the liquid becomes turbid. On further heating this disappears, and the formation of crystals begins. As soon as these separated the solution was filtered while still warm, in order that any γ -compound remaining might be held in solution. This crystallization was repeated, until the dried crystals

when treated with gaseous ammonia neither changed their color nor gave a fluorescent solution on the addition of water. The crystals thus obtained were mostly a mixture of more or less brownish needles and orange-colored leaflets, which, however, in both cases were pure β -orcinolphthalein (see p. 1227). In order to obtain them all as needles a dilute (1 : 20) alcoholic solution of the phthalein is run while hot into ten times the amount of cold water, and digested on the water bath till the milky white turbidity has been converted into clusters of microscopic needles. If, on the other hand, the phthalein be dissolved in ten times the amount of hot alcohol, one-half the volume of water added to this, and the solution boiled, fairly large, orange-colored, six-sided plates separate. These lose no water *even at* 205° , and decompose at higher temperatures. Although this residue gave data on combustion in agreement with the formula for the anhydrous phthalein, the authors state: "dieselbe kann aber unter den obwaltenden Umständen kaum als entscheidend angesehen werden." Four other combustion analyses are given, 1 and 2 are on the leaflets obtained by the addition of water to the alcoholic solution, 3 is on the amorphous material precipitated from the alkaline solution by sulfuric acid, and finally 4 is on the phthalein recovered from the β -phthaleindibenzoate, and which had been dissolved in alcohol and crystallized by heating with water. In 1 and 2 the substance was dried in a xylol bath, and in 3 and 4 in an aniline bath. The analyses agree with the formula $C_{22}H_{16}O_6 \cdot \frac{1}{2}H_2O$ (see p. 1428).

Calculated: C, 72.13; H, 4.55; found: C (1) 72.01, (2) 72.10, (3) 71.98, (4) 72.13; H, (1) 4.50, (2) 4.49, (3) 4.23, (4) 4.37.

These analyses are in agreement with those given by E. Fischer for his "*monoacetate*" (see p. 1202), and the following observations according to R. and H. Meyer also prove the identity of the two: If the needle-shaped crystals of the β -phthalein be dissolved in glacial acetic acid by gently warming, then on cooling almost colorless needles separate; if, on the other hand, the solution be boiled strongly, yellowish red leaflets crystallize out on cooling. From dilute alkaline solutions this phthalein is thrown down as a *white* precipitate by acetic acid (see p. 1229).

The β -phthalein does not show a definite melting point. It is easily soluble with a brown color in methyl and ethyl alcohols, and in ethyl acetate, difficultly soluble in hot water, benzene or glacial acetic acid. Ether dissolves the amorphous substance easily. It dissolves in caustic alkalies and their carbonates, as well as in ammonia, with an intense cherry-red color, which even in extreme dilution does not disappear on shaking with ether. Mineral acids precipitate the free phthalein out of this solution in yellow flocks. Solutions of sodium phosphate or sodium acetate also dissolve it, on warming, with a cherry-red color, but this color disappears on shaking with ether, which takes up the phthalein.

With fuming hydrochloric acid the β -phthalein forms a deep red addition product insoluble in hydrochloric acid similar to that of the α -isomer (see p. 1205).

Tetrabromo- β -orcinolphthalein was obtained by boiling the β -phthalein with glacial acetic acid and the calculated amount of bromine. Brown crystals separated. These were washed with alcohol, dissolved in sodium hydroxide, precipitated with sulfuric acid, the precipitate washed with water, and extracted with alcohol. The white crystalline residue gave, on recrystallization from hot nitrobenzene, irregular colorless plates. These gave results on analysis agreeing with the formula $C_{22}H_{12}Br_4O_6$. It dissolves with difficulty in all solvents except hot nitrobenzene. Caustic alkalis and the alkali carbonates dissolve it with a greenish black color; when very dilute this solution shows by transmitted light a smudgy red color. R. and H. Meyer point out that this description agrees so well with that given by Emil Fischer (see p. 1202) for his tetrabromo-orcinolphthalein that there can be no doubt that it was actually the tetrabromo- β -orcinolphthalein with which he was working. The substance is not a dye. Gaseous ammonia does not act on it, and hence it may be easily isolated from a mixture of tetrabromo- β - and - γ -orcinolphthaleins (see p. 1232).

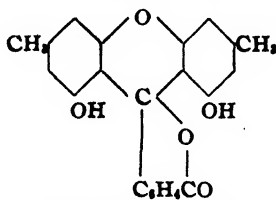
γ -Orcinolphthalein.—To isolate this body the crude product was treated with gaseous ammonia, extracted with water, and the resulting solution allowed to stand in the air for some time, when some β -phthalein precipitated. This was filtered off and from the filtrate the γ -phthalein was precipitated by sulfuric acid. This was washed with hot water, dissolved in ammonia, alcohol added, the solution acidified with sulfuric acid and steam passed into the milky solution to remove the alcohol. On cooling, tolerably large, pale yellow prisms separated. From hot, concentrated, glacial acetic acid solution dark orange-colored crystals separated on cooling. The analyses of the two products dried at 180° were in accord with the formula $C_{22}H_{16}O_5$ (see p. 1235).

The γ -orcinolphthalein is easily soluble with a brown color in alcohol, methyl alcohol, and hot glacial acetic acid. From dilute alcohol it separates on slow evaporation in bright yellow clusters of broad, truncated needles. It exhibits the greatest analogy to fluorescein. When precipitated in the amorphous form it is deep yellow colored, and dissolves in alkalis, ammonia, and their carbonates with a brown color and greenish fluorescence. This is not so intense as in the case of fluorescein, but is considerably increased by the addition of alcohol. The substance dyes silk yellow. It dissolves on heating in sodium phosphate and sodium acetate solutions, presumably due to the formation of the sodium salt (as in the case of fluorescein). These solutions fluoresce, and are not decolorized on shaking with ether (distinction from β -orcinolphthalein). On boiling with calcium carbonate, carbon dioxide is expelled and the

substance goes into solution as the calcium salt. When boiled with hydrochloric acid or dilute sulfuric acid small amounts of it dissolve with a yellow color. The amorphous substance is easily soluble in ether with a yellow color and without fluorescence. The ammonium salt forms readily under the action of gaseous ammonia, as mentioned above. The ammonia passes off completely from this compound, however, on long exposure to the air.

In his paper on "Untersuchungen über die Abkömmlinge des Triphenylcarbinols,"¹ Baeyer gave some attention to the α -orcinolphthalein of R. Meyer. As will be shown below he concludes that in this isomer the hydroxyl groups occupy the positions ortho to the methane carbon atom. He proposes to replace the designation α - with the term vicinal, since it is customary to designate the volatile nitroresorcinol of Kauffman in which the nitro group occupies an analogous position as vicinal nitroresorcin. The mother substance, which has, however, not yet been made, would then be designated as *vic*-resorcinolphthalein, and likewise the triphenylcarbinol derivative as *vic*-resorcinolbenzein. For the β -orcinolphthalein of R. Meyer which is an intermediate product between the vicinal and the ordinary form, he proposes the term semi-vicinal, to be shortened to "semi-vic," while the γ -substance is to be designated simply as orcinolphthalein.

According to Baeyer the *vic*-orcinolphthalein corresponds so exactly in its conduct to the *vic*-nitroresorcinol, that it must possess the structure given below:



Vic-orcinolphthalein.

He calls attention to the fact that Meyer's statement (see p. 1205) "Beim Vermischen einer alkoholischen Lösung des Phtaleins mit alkoholischen Kali, bildet sich ein in alkohol unlösliches blaues Kaliumsalz, das in kleinen bronzeglänzenden Nadelbüscheln ausfällt" is incomplete. According to Baeyer, if a little alcoholic potash be added to an alcoholic solution of the vicinal orcinolphthalein, the solution is at first colored violet, but this soon disappears, and a potassium salt separates in colorless, elongated, right-angled plates. This salt, Baeyer states, may be used advantageously for the complete separation of the vicinal orcinolphthalein from its isomers. For if it be heated with a large amount of water the salt is decomposed by hydrolysis into the free orcinolphthalein and into alkali, which holds a small part of the vicinal orcinolphthalein and all of

¹ *Ann. (Liebig)*, 372, 120 (1910).

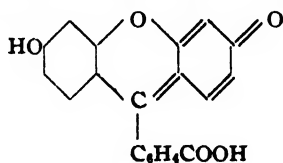
its isomers in solution. The *vic*-orcinolphthalein when filtered off is pure white, and is completely extracted from its red solution in soda on shaking with ether.

If more alcoholic potash be added to the solution of the phthalein (from which the white crystals of the potassium salt have separated), and the solution be boiled it becomes a deep reddish violet, and crystals separate which appear black under the microscope, but which possess the same forms as the white, *i. e.*, are apparently pseudomorphs. If, however, the alcoholic solution of the phthalein be added to an excess of alcoholic potash heated to boiling, black needles, obliquely truncated, separate. Besides these, blue, transparent leaflets are also formed.

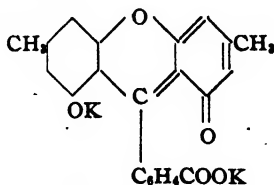
When the white crystals are boiled with soda solution, there separates on cooling, hair-like needles of a violet color, but, if they are warmed with concentrated potassium hydroxide, the liquid becomes pure blue. On dilution the solution turns violet.

From this Baeyer concludes that there are at least three kinds of salts, a white, a red, and a blue, the formation and composition of which he accounts for in the following manner:

From the formula for the vicinal orcinolphthalein (see p. 1208), it would be simplest to assume that, in the first place, the hydrogen atoms of the two hydroxyl groups are replaced by metal. Such a salt must, however, be colorless. Since now a violet color first appears, it is to be assumed that in the first place the rupture of the lactone ring takes place with the formation of a violet salt, corresponding to fluorescein, which, however, contains instead of a para- an ortho-quinoid group.

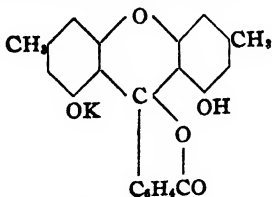


Fluorescein.



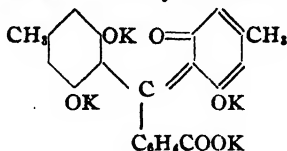
First violet salt.

This first violet salt changes into the colorless, monopotassium salt of the phthalein through reformation of the lactone ring, which, as the decolorization of an alkaline solution by means of ether shows, takes place very readily in the case of the vicinal orcinolphthalein.



Colorless salt.

On the addition of more alkali the lactone group is broken again, and there is formed in consequence of this a tertiary alcohol, to the active nature of which is to be attributed the rupture of the xanthone ring. That this rupture actually takes place even at ordinary temperature is shown by the analysis of the colored potassium salt, according to which it contains between 3 and 4 atoms of potassium. This is possible, however, only on the assumption of the hydrolytic cleavage of the oxygen bridge. The colored salt containing four atoms of the metal can only have the following constitution because of the symmetrical structure of the orcinol:

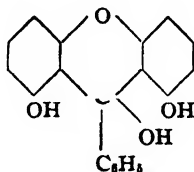


since it is immaterial, whether the hydroxyl already present or that formed from the bridge oxygen becomes quinoid. Analyses of the potassium salts (see pp. 1222 to 1227):

1. Colorless potassium salt:¹ calc. for $C_{22}H_{14}O_6K_3$: K, 17.89; for $C_{22}H_{14}O_6K$: K, 9.37; found: K, 13.64.

2. Blue potassium salt: calc. for $C_{22}H_{14}O_6K_4$: K, 29.43; found: K, 27.05.

In regard to the analogy between phenyl-2,2'-dioxyxanthanol (*vic*-resorcinolbenzein)



and α -orcinolphthalein Baeyer says:²

"Aus der Identität der Färbung, welche das Chlorid in Alkalischer Lösung zeigt, mit der des α -orcinphthaleins von R. Meyer, geht hervor, dass letzteres wirklich, wie angenommen, *vic*-orcinphthalein ist."

Recently Kehrman³ has prepared ethers and esters of the phthaleins and benzeins of orcinol with a view to studying their oxonium salts.

In order to completely free the β -phthalein from the tenaciously adhering γ -isomer, Kehrman dissolves the crude β -compound (isolated according to the method of R. and H. Meyer) in boiling alcohol, adds a few drops of ammonia, and then boiling water until the solution becomes

¹ The formula for the monopotassium salt is $C_{22}H_{14}O_6K$, and according to 1915 atomic weights contains 9.82% potassium; that of the dipotassium salt $C_{22}H_{14}O_6K_2$, and 17.92% potassium; that of the tetrapotassium salt $C_{22}H_{14}O_6K_4$, and 29.48% potassium. The tripotassium salt of the *carbinol carboxylic acid*, $C_{22}H_{14}O_6K_3$, contains 23.82% potassium (see p. 1227).

² *Ann.* (Liebig), 372, 133 (1910).

³ *Ber.*, 45, 3505 (1912).

turbid. During the cooling the β -isomer crystallizes out, while the mother liquor shows the presence of the γ -compound by its fluorescence. Repeated three times this method gave a product which no longer yielded a fluorescent mother liquor when treated in this manner, and was, therefore, certainly free from the γ -isomer.

Kehrmann states that β -orcinolphthalein exists in *two modifications*, a *yellow quinoid*, and a *colorless lactoid form*, and he adds in a footnote that R. and H. Meyer had already observed both modifications, but that it was not quite certain whether their product was perfectly free from the γ -isomer (see p. 1228). Acidification in the cold of the dark brownish red alkaline solution gives, according to him, an orange yellow precipitate, which when heated to boiling becomes perfectly white. The lactoid form is here the stable one, while the salts, those with alkalies as well as those with acids, are derived from the quinoid modification, which is unstable in the free condition (see p. 1229). The latter form becomes the stable one, however, by esterifying the carboxyl or by replacing it with hydrogen, as the study of γ -orcinolbenzein has shown.

In order to completely free the γ -isomer from traces of the tenaciously adhering β -derivative, Kehrmann states that treatment of the crude product with methyl alcohol and hydrochloric acid was found to be very advantageous. The hydrochloride, which separated quite completely in bright orange-yellow leaflets having a bluish reflection, was chemically pure. In a footnote he states that the base exists in a yellow and in a colorless form (see p. 1234).

Experimental.

The investigation of the orcinolphthaleins and of the orcinoltetrachlorophthaleins was undertaken (1) to study the effect of introducing negative groups into the phthalein molecules; (2) to observe to what extent these compounds and their derivatives exist in colored and colorless modifications, and to see whether these forms are in agreement with the theory of color held by chemists at the present time; and (3) to study the conditions affecting the formation of the different isomers, and the methods of separating these, thus throwing possible light on the problem of the isomeric fluoresceins.¹

At the outset some difficulty was encountered in preparing the orcinoltetrachlorophthaleins (see p. 1239). This difficulty, together with the fact that R. and H. Meyer had not carefully studied the colored and colorless forms of the orcinolphthaleins, and had omitted certain important derivatives prompted the repeating and enlarging of the major part of the work previously done on these phthaleins.

The phthalic anhydride used in this work was pure sublimed material. The orcinol obtained from Merck was pure and had a melting point of

¹ THIS JOURNAL, 36, 680 (1914).

58°. It was freshly fused before using. The fused material¹ melted sharply at 107°.

In the preparation of the orcinolphthaleins the directions of E. Fischer were first employed. Fifty grams of phthalic anhydride, 85 g. of orcinol, and 45 cc. of concentrated sulfuric acid were placed in a flask and heated to 135° for two hours. The mass became semi-liquid, and red colored, but did not solidify toward the end of the reaction. It was poured into water, the yellowish incoherent mass filtered, washed, and the filtrate preserved for the recovery of unchanged orcinol. The material was then dissolved in alkali, the solution filtered, the phthaleins precipitated as a yellowish flocculent mass with acetic acid, and the mixture heated to boiling by blowing in steam. The material darkened slightly and showed a tendency to collect in pasty masses. The anhydrous material weighed 104.5 g., corresponding to 85.9% of the theory, calculated from the amount of phthalic anhydride used.

Fifty grams of this material were purified (see pp. 1216 and 1217) and the following amounts of isomers obtained:

| Isomer. | Grams. | Percentage. |
|----------------|--------|-------------|
| α | 10.0 | 23.0 |
| β | 27.0 | 62.2 |
| γ | 5.4 | 12.5 |
| Tar..... | 1.0 | 2.3 |
| Total..... | 43.4 | 100.0 |

The use of phosphorus pentoxide at 135° as a condensing agent was next tried. One hundred grams phthalic anhydride, 170 g. orcinol, and 170 g. phosphorus pentoxide were placed in a flask and heated to 135° for two hours. The dark red mass was ground, dissolved in alkali, and the solution filtered. The phthaleins were then precipitated by adding dilute sulfuric acid, and the mixture heated to boiling with steam, filtered and washed in the usual manner. This product differed markedly from that of the previous fusion in that it became dark, almost black, on heating to boiling with steam, and collected in a sticky mass which on drying became hard and brittle. The crude anhydrous material weighed 140 g., corresponding to 57.5% of the theory.

Fifty grams of this material were purified, and resolved into its isomers:

| Isomer. | Grams. | Percentage. |
|----------------|--------|-------------|
| α | 5.0 | 11.9 |
| β | 21.0 | 50.0 |
| γ | 14.0 | 33.3 |
| Tar..... | 2.0 | 4.8 |
| Total..... | 42.0 | 100.0 |

The synthesis was repeated, keeping the temperature between 180° and 190°. The material from this fusion was purified as usual. It was precipitated from the alkaline solution as yellow flocks by the addition of mineral acids. On heating this mixture to boiling with steam the material became dark colored and collected in a pasty mass.

¹ The statement of Hesse, *J. prakt. Chem.*, [2] 57, 270, that the melting point of anhydrous orcinol is 100–101°, is certainly incorrect. We have determined this melting point many times and on large quantities of material, and have invariably found it to be 107°.

Fifty grams phthalic anhydride, 87 g. of fused orcinol and 90 g. of P_2O_5 gave 87 g. of anhydrous material corresponding to a yield of 71.5%.

Fifty grams of this material gave on purification:

| Isomer. | Grams. | Percentage. |
|----------------|--------|-------------|
| α | 5.7 | 13.2 |
| β | 22.0 | 50.9 |
| γ | 14.0 | 32.4 |
| Tar..... | 1.5 | 3.5 |
| Total..... | 43.2 | 100.0 |

Sulfuric acid at a high temperature was then used as a condensing agent. The bath was heated to 180–190°, and the flask containing 25 g. phthalic anhydride, 43 g. orcinol, and 23 cc. of concentrated sulfuric acid was immersed in it for two hours. The reaction was vigorous, and was accompanied by boiling. The temperature of the mixture showed a tendency to rise above 180° as a result of the heat of the violent reaction. A too high rise was avoided by removing the flask occasionally from the bath. The melted mass was poured into water, and purified in the usual manner. The phthalins were precipitated from the alkaline solution with sulfuric acid as yellow flocks, which when heated to boiling by blowing in steam darkened but slightly, and showed but little tendency to form pasty masses. The yield of anhydrous material was 92.5%. The entire product (55.5 g.), gave the following amounts of the different isomers:

| Isomer. | Grams. | Percentage. |
|----------------|--------|-------------|
| α | 14.7 | 28.2 |
| β | 29.4 | 56.4 |
| γ | 7.6 | 14.6 |
| Tar..... | 0.4 | 0.8 |
| Total..... | 52.1 | 100.0 |

Meyer states that (see p. 1204) glacial phosphoric acid gives a larger yield of the γ -isomer. This substance was therefore used as a condensing agent. Twenty grams phthalic anhydride, 39 g. orcinol, and 60 g. glacial phosphoric acid were ground together and heated. The reaction took place very slowly even at 195–200°. At the end of two hours the heating was discontinued and the fused mixture freed from unchanged orcinol, phthalic anhydride, and inorganic materials in the usual manner. On heating to boiling with steam the product was obtained as a black, tarry mass, which on drying became hard and brittle. The anhydrous material (27.6 g.) corresponded to a yield of 56.7% of the theory (see p. 1215).

A smaller amount of phosphorus pentoxide was next tried to see if the production of tar could be avoided. Twenty grams phthalic anhydride, and 34 g. orcinol were fused at 180°, and the condensing agent, 13 g. P_2O_5 , then added. The temperature was maintained at 180° for two hours, and the product of the fusion was purified in the usual manner. Upon the addition of an acid to an alkaline solution of the crude material a yellowish brown flocculent precipitate was obtained which blackened and formed a pasty mass on heating to boiling. A yield of only 52.8% was obtained by this method. The experiment failed, therefore, to accomplish the desired end.

The experiment was repeated at a temperature of 120°. While the crude product was free from tar, *i. e.*, precipitated as yellow flocks, which remained unchanged on heating to boiling, only 9 g. corresponding to a yield of 18.5%, was obtained. On separation this product yielded the following amounts of isomers:

| Isomer. | Grams. | Percentage. |
|----------------|--------|-------------|
| α | 1.2 | 13.8 |
| β | 5.0 | 57.5 |
| γ | 2.5 | 28.7 |
| Total..... | 8.7 | 100.0 |

The experiment was again repeated but the temperature maintained at 135°. The crude anhydrous phthaleins which contained some tar, weighed 15 g., corresponding to a yield of 30.8%.

Fuming sulfuric acid was next tried as a condensing agent. Twenty grams phthalic anhydride, 34 g. orcinol, and 18 cc. fuming sulfuric acid (15% SO₃) were used. The first two were fused at 120°. The fuming sulfuric acid was then added, and a vigorous reaction took place at once, accompanied by change of color, boiling, and evolution of steam. The flask was quickly removed from the bath, but the temperature continued to rise, finally reaching 200°, but on being left to stand at room temperature returned to 120° in 20 minutes. The flask was then replaced in the bath and the temperature of the contents held at 120° for two hours. The melted mass, which showed no tendency to solidify, was poured into water. The lumps which formed at once were easily broken up, and the whole mass soon became yellow and pulverulent. When dissolved in alkali and subsequently precipitated with mineral acids it separated as bright yellow flocks, which on heating to boiling with steam did not change in the least, *i. e.*, it was perfectly free from tar. The material was filtered off, washed, and dried to constant weight in the water oven. After this treatment it weighed 47.5 g., 97.9% of the theory.

The product was next resolved into its isomers by the usual method. It was found to be so nearly free from tar that on filtering the ether solution (see p. 1217) only enough was present to color the filter paper slightly. The entire 47.5 g. gave:

| Isomer. | Grams. | Percentage. |
|----------------|--------|-------------|
| α | 11.7 | 27.4 |
| β | 25.0 | 58.5 |
| γ | 6.0 | 14.1 |
| Total..... | 42.7 | 100.0 |

This synthesis was repeated using the same amounts of materials. The reaction took place slowly even at room temperature, the contents of the flask turning red, and the temperature in a few minutes rising to 75°. The flask was then immersed in boiling water for four hours. The content was stirred by an occasional shaking. The purification was carried out exactly as in the preceding experiment, and the product was exactly similar in all respects. The anhydrous material weighed 47.5 g., 97.9% of the theory. Separated into its isomers the following results were obtained:

| Isomer. | Grams. | Percentage. |
|----------------|--------|-------------|
| α | 11.0 | 25.9 |
| β | 25.0 | 58.8 |
| γ | 6.5 | 15.3 |
| Total..... | 42.5 | 100.0 |

Zinc chloride was finally used as a condensing agent. Twenty grams phthalic anhydride, 34 g. orcinol, and 34 g. freshly fused zinc chloride were intimately ground in a mortar, transferred to a flask, and heated to a temperature of 120° for two hours. The mass became red in color and semi-liquid, and at the end of two hours had partially solidified. Purified as in previous cases the material (24.7 g.) was found to be practically free from tar. The yield was, however, only 50.8% of the theory.

SUMMARY OF IMPORTANT SYNTHESIS.

| Condensing agent. | Temperature. | Crude yield. % | Percentage Isomers. | | |
|--|--------------|----------------|---------------------|-----------|------------|
| | | | α . | β . | γ . |
| P ₂ O ₅ | 135° | 57.5 | 11.9 | 50.0 | 33.3 |
| P ₂ O ₅ | 180° | 71.5 | 13.2 | 50.9 | 32.4 |
| P ₂ O ₅ | 120° | 18.5 | 13.8 | 57.5 | 28.7 |
| H ₂ SO ₄ | 135° | 85.9 | 23.0 | 62.2 | 12.5 |
| H ₂ SO ₄ | 180° | 92.5 | 28.2 | 56.4 | 14.6 |
| H ₂ S ₂ O ₇ | 120° | 97.9 | 27.4 | 58.5 | 14.1 |
| H ₂ S ₂ O ₇ | 95° | 97.9 | 25.9 | 58.8 | 15.3 |

These results show that from the standpoint of crude yield and purity of product, fuming sulfuric acid is the best condensing agent, concentrated sulfuric acid, and phosphorus pentoxide following in the order named. The last gives a relatively higher percentage of the γ -phthalein, and if it could be used in such a manner as to give a good yield without the production of tar, it would be the most desirable condensing agent to use for the preparation of the γ -compound. Glacial phosphoric acid is very nearly worthless; evidently the statement of R. and H. Meyer in regard to the use of this substance is a typographical error. Zinc chloride, if used, must be employed for a longer period than two hours or at a higher temperature than 120°.

A critical study of the methods of isolating the isomers was also made. After a large number of experiments, testing the methods described in the literature for the separation of such isomers, and also such methods and modifications as seemed most promising, a fairly satisfactory method was developed. At the outset it was found that some of the methods used by Meyer in separating the phthaleins were slow, or gave incomplete separation; or both, and had to be modified or abandoned. For instance, the method he used for extracting the γ -phthalein (see p. 1207) was found to be unsatisfactory because (1) not all of the γ -phthalein was removed from the crude product, and (2) some β -phthalein was always carried through into the ammoniacal filtrate, which upon standing for some time was precipitated as a colloidal mass that could not be removed by filtration. This difficulty had been previously noted by Acker¹ and the method was abandoned by him. Meyer's separation of the γ - and β -isomers was therefore incomplete.

Even less complete was Meyer's separation of the α - and β -compounds. He extracted the residue obtained after removal of the γ -phthalein by means of cold soda solution or with dilute ammonia until the washings were blue-red instead of the cherry-red color first obtained. A critical examination of this method showed that it was unsatisfactory for two reasons; first, the β -phthalein was very slowly removed, and so large a number of extractions were necessary that the method was laborious, the more so as

¹ Diplom-Arbeit, Chemie-Schule in Mülhausen i/E, 1910.

with each extraction with soda the solutions became more and more difficult to filter, due to the fact that the tarry material gradually became gelatinous under the influence of the alkali; and secondly, not inconsiderable amounts of α -phthalein were carried into the soda solution.

The method of Kehrmann for separating the γ - from traces of the β -isomer gave better results than that employed by Meyer. As mentioned above (see p. 1211) Kehrmann dissolved the crude material in methyl alcohol and passed in hydrochloric acid gas, keeping the solution at 0° , whereupon the γ -hydrochloride separated in the pure state. The last traces of the γ -compound were removed from the β -phthalein by dissolving the latter in alcohol, adding a few drops of ammonia, heating to boiling, and adding hot water until the solution became turbid. On cooling the pure β -compound crystallized out (see p. 1210). It remained then to develop a method for separating the α - from the β -compound. To accomplish this, advantage was taken of the difference in behavior of an ethereal solution of these isomers toward dilute soda solution. Meyer states that the soda solution of the α -isomer is decolorized on shaking with ether, or remains only pale bluish red. Baeyer states, however, that the soda solution of the α -compound is completely decolorized by shaking with ether. The latter statement was found to be more nearly correct, although if an ethereal solution of the α -phthalein be shaken with soda solution some color is imparted to the latter, unless the ethereal solution be quite dilute. Meyer states that the soda solution of the β -phthalein is not decolorized by ether. While this is true, a large part of the phthalein does go into the ethereal layer. On the other hand an ethereal solution of the β -isomer gives up part of its phthalein to sodium carbonate solutions, and by successively removing the latter all the β -compound can be removed from the ether.

To separate the α - from the β -isomer, the mixture of the freshly precipitated phthaleins is dissolved in ether. This ethereal solution is *filtered* and then shaken with normal sodium carbonate solution when some of the β - and a much smaller amount of the α -phthalein goes into the soda solution. This latter solution is now removed and shaken with a small portion of *fresh* ether which removes *all* the α - and a little of the β -phthalein, leaving only the β -isomer in the soda solution. After removing the sodium carbonate solution from the original ether solution, it is again extracted with fresh soda solution, the latter drawn off and shaken with the *same smaller portion of ether* that was used to extract the first soda solution. This process of extraction is repeated until a fresh portion of the soda solution when shaken with the original ether solution is only faintly colored, and this color is at once removed when the soda solution is shaken with the smaller portion of ether. The α -phthalein is now found in the ether solutions while the several soda solutions will contain only the β -compound.

For a 50 g. portion of the crude orcinolphthaleins two liters of ether in a four liter separatory funnel are used for the main ethereal solution. The smaller portion of ether is usually about 500 cc. while the portions of normal soda solution used for extraction are usually about 300 to 500 cc.

Another very important step in the purification was the removal of tarry material from the crude product. To do this advantage was taken of the very great solubility of the freshly precipitated phthaleins in ether, and of the relative insolubility of the tar in this solvent.

The method used in separating and purifying the three isomers was as follows: The cold filtered alkaline solution of the crude product is precipitated by pouring slowly into a large volume of dilute *mineral* acid (acetic acid is not suitable here because on subsequent shaking with ether it is taken up by the latter to some extent, and reduces the solubility of the phthaleins in this solvent). The mixture of the freshly precipitated phthaleins and water is shaken up in a large separatory funnel with a large amount of ether, allowed to stand until the two layers have sharply separated, when the tarry by-products collect in a flocculent dark-colored mass between the two layers. The aqueous layer is then removed, and the ether filtered (first through muslin and then through filter paper). The clear ether solution is now shaken with about one-third of its volume of normal soda solution, the two layers allowed to separate, and the aqueous one removed. This contains all the γ - except traces, considerable β -, and some of the α -phthalein. The last and most of the β -compound are removed by shaking the soda solution with fresh portions of ether, and the α - and β -phthaleins are separated as outlined above. The γ -phthalein and a little of the β -product remaining in the soda solution are recovered by acidification and the γ -isomer purified by the hydrogen chloride method of Kehrman. For final purification of the β -phthalein, the alcoholic ammonia method of Kehrman is used.

α -Orcinolphthalein.

Compound with Methyl Alcohol.—The crude α -orcinolphthalein obtained by the method of separation outlined above is quite pure, and when precipitated from its alkaline solution by acetic or a mineral acid, it separates in the form of *pure white* flocks. It can be crystallized quite readily from methyl or ethyl alcohol, or from glacial acetic acid. As a rule the material for experimental work was crystallized from methyl alcohol, then from glacial acetic acid, and finally from dilute warm solutions in methyl and in ethyl alcohols by the addition of water. In the latter cases, that is, when water was added to the dilute solution in either of the alcohols, perfectly white, nearly rectangular plates were obtained. The pure white material from the methyl alcohol solution was analyzed:

Subst. (I) 0.1186, (II) 0.2430; loss, (I) 0.0098, (II) 0.0195. Calc. for $C_{22}H_{18}O_6$.— CH_3OH : 8.17; found: (I) 8.26, (II) 8.02.

Sample I had been dried in the air for about 20 hours. It lost all its alcohol in one-half hour at 110° , and nothing condensed on the cool part of the tube,¹ i. e., it contained no water. It lost no further weight on heating to 180° . Sample II was dried in the air for about 10 days and then heated in the electric drying apparatus² for one-half hour at 185° . Hence α -orcinolphthalein crystallizes from methyl alcohol with a molecule of methyl alcohol.

The residue obtained in determination II was analyzed.

Subst., 0.1003; CO_2 , 0.2691; H_2O , 0.0409. Calc. for $\text{C}_{22}\text{H}_{18}\text{O}_6$: C, 73.31; H, 4.48; found: C, 73.17; H, 4.57.

α -Orcinolpthalein is insoluble in water, but easily soluble in dilute caustic alkalies with a beautiful purplish red color, the alkaline salts possessing a high tinctorial power. It dissolves with difficulty in aqueous ammonia, and in solutions of the alkaline carbonates it dissolves only on warming. The solutions in these weak alkalies are *wine-red*, not *purplish red*. Dry ammonia gas and dry hydrochloric acid gas do not act on the α -phthalein. In the more concentrated (50%) solutions of the caustic alkalies it dissolves with a pure *blue* color. From all alkaline solutions the free phthalein is thrown down on the addition of acids as white flocks. It is quite soluble in methyl and ethyl alcohols and in glacial acetic acid, and is very soluble in acetone. It is insoluble in benzene. When perfectly pure it dissolves in an alcoholic solution of ammonia *without color*. When this solution is diluted with water it becomes *reddish violet* and after a time the α -phthalein crystallizes out and the solution becomes *colorless*. The slightest trace of β - or γ -phthalein can thus be detected in the α -phthalein (see pp. 1228 and 1234).

Compound of α -Orcinolpthalein with Ethyl Alcohol.— α -Phthalein, shown to be pure by the above analysis, was dissolved in hot absolute alcohol, and the solution then allowed to cool. The fine crystals which separated during the cooling were filtered off, and the mother liquor allowed to stand two days longer. Large, well formed, colorless prisms slowly formed. These were filtered off, and water added to the mother liquor. Minute colorless crystals separated, which under the microscope were seen to possess the same form as the large ones. A sample of each crop when heated at 170° came to constant weight in one-half hour, and during the heating no moisture condensed on the cool part of the tube. The following results were obtained:

Subst., (I) 0.4793, (II) 0.4871; loss (I) 0.0545, (II) 0.0526. Calc. for $\text{C}_{22}\text{H}_{18}\text{O}_6 \cdot \text{C}_2\text{H}_5\text{OH}$: 11.34; found: (I) 11.37, (II) 10.80.

Determination I was on the phthalein crystallized from absolute alcohol on long standing, while II was on the material obtained by addition of

¹ *Am. Chem. J.*, 41, 404 (1909).

² *THIS JOURNAL*, 32, 635 (1910); *Am. Chem. J.*, 48, 477 (1912).

water to the mother liquor. The phthalein therefore crystallizes with one molecule of ethyl alcohol.

Compound of α -Orcinolphtalein with Acetic Acid.—Some of the pure α -phthalein was dissolved in boiling glacial acetic acid, and the hot solution quickly filtered. On cooling a large crop of white, well formed, stout needles separated. These were filtered off and allowed to stand in the air for two days, when all odor of acetic acid had disappeared. A portion was then finely ground and analyzed.

Subst., 0.4069; loss, 0.0653. Calc. for $C_{22}H_{16}O_6 \cdot CH_3COOH$: 14.29; found: loss 16.05.

The sample came to constant weight when heated for one hour at 175° . In order to determine the acetic acid actually present, a weighed amount of the sample was boiled with distilled water and after filtration the free acid in the solution was titrated with standard alkali using phenoltetrachlorophthalein as the indicator.

Subst., (I) 0.7844, (II) 1.1930, (III) 0.6985; 0.1 *N* NaOH, (I) 20.57, (II) 30.00, (III) 14.67 cc. Calc. for $C_{22}H_{16}O_6 \cdot CH_3COOH$: 14.29; found: (I) 15.74, (II) 15.10, (III) 12.61.

Sample I was analyzed immediately after grinding, II, 5 hours, and III, 72 hours after grinding. The phthalein therefore crystallizes with a molecule of acetic acid.

α -Orcinolphtalein Diacetate.—Fifteen grams of pure α -phthalein were boiled for one hour with an equal weight of anhydrous sodium acetate and seven times its weight of acetic anhydride. When the material was poured into cold water it separated as a colorless oil. After this had solidified, the supernatant liquid was decanted and the solid material triturated with cold normal sodium hydroxide solution, filtered off, washed and dried. It was first crystallized from absolute alcohol, from which solvent it separated in perfectly white, well-formed, stout prisms. In the melting point tube the material shrinks markedly above 230° , and finally melts sharply at $246\text{--}247^\circ$, incipient decomposition being indicated at slightly higher temperatures by the production of a greenish color. Recrystallized from ethyl acetate it formed the same type of crystals, which behaved in the same manner in a melting point tube, and melted sharply at $246\text{--}247^\circ$. It was finally crystallized from benzene and gave a melting point of $246\text{--}247^\circ$. A sample of this material heated for one-half hour at 180° , lost 2.78% (benzene of crystallization). The material left was then analyzed.

Subst., 0.1404; CO_2 , 0.3627; H_2O , 0.0594. Calc. for $C_{22}H_{16}O_6(COCH_3)_2$: C, 70.25; H, 4.54; found: C, 70.45; H, 4.73.

α -Orcinolphtalein diacetate is insoluble in water, and in the alkalis, soluble in benzene and rather sparingly soluble in alcohol, and in ethyl acetate. It is readily saponified by alcoholic potash.

α -Orcinolphtalein Dibenzoate.—Five grams of pure α -phthalein

were dissolved in dilute alkali in a bottle, 10 g. benzoyl chloride added, the bottle stoppered and the contents shaken vigorously for some time. Benzoyl chloride and strong alkali were added from time to time as necessary, and the shaking continued till the mixture was only slightly violet colored. The slightly yellowish, somewhat oily product was stirred up with soda solution, filtered and allowed to dry in the air. It crystallized from hot benzene in fine, white needles which melted at 276° . Recrystallized from absolute alcohol it melted at 277° . The melting point is not changed by recrystallizing from benzene. Meyer gives the melting point of this derivative as 284° . For analysis a sample was heated to constant weight at 180° for one-half hour.

Subst., 0.1060; CO_2 , 0.2958; H_2O , 0.0435. Calc. for $\text{C}_{22}\text{H}_{14}\text{O}_5(\text{COC}_6\text{H}_5)_2$: C, 76.03; H, 4.26; found: C, 76.11; H, 4.59.

The dibenzoate is insoluble in water and in alkalies. Aqueous alkalies do not saponify it perceptibly in the cold, and only with difficulty on warming; alcoholic potash acts more rapidly, but still more slowly than it does on the diacetate. The dibenzoate is soluble in hot benzene, and in hot acetone, and rather difficultly soluble in hot absolute alcohol.

Tetrabromo- α -orcinolphthalein.—To 10 g. of pure α -phthalein in 125 cc. of glacial acetic acid 22 g. of bromine in 50 cc. glacial acetic acid were added dropwise with constant shaking. After standing over night the pale yellow powder was filtered off and extracted with boiling absolute alcohol. The air dried material weighed 17 g., corresponding to a yield of 90%. Five grams of this material were used in preparing the acetyl derivative (see p. 1221), and the rest dissolved in alkali by heating to boiling, filtered and precipitated by pouring into dilute hydrochloric acid. The tetrabromo compound separated as slightly colored gelatinous flocks, which on heating became very nearly white. Filtered, dried, and extracted with boiling alcohol the material was obtained as a colorless powder. The compound thus prepared agrees with the description of tetrabromo- α -orcinolphthalein prepared by Meyer (see p. 1207). It dissolves only partly in cold alkali, and on cooling the hot alkaline solution a dark-colored product slowly separates. A portion of the amorphous material was heated to constant weight at 180° and analyzed.

Subst., (I) 0.4048, (II) 0.5122; 0.1 N AgNO_3 , (I) 21.41, (II) 27.08 cc. Calc. for $\text{C}_{22}\text{H}_{12}\text{O}_4\text{Br}_4$: Br, 47.31; for $\text{C}_{22}\text{H}_{12}\text{O}_4\text{Br}_3$: Br, 39.12; for $\text{C}_{22}\text{H}_{12}\text{O}_4\text{Br}_2$: Br, 40.17; found: Br, (I) 42.27, (II) 42.25.

The compound therefore loses bromine, in the alkaline solution, since the diacetate (see p. 1221) prepared from the same tetrabromo- α -orcinolphthalein analyzed in agreement with the theory. It evidently loses bromine quite easily, since the alkali used was only a little stronger than normal. The preparation was repeated.

The pale yellow powder was seen under the microscope to consist of well

formed rectangular prisms. These were extracted with 200 cc. of boiling benzene which removed nearly all the color, and then with acetone, whereupon a *perfectly white product* was obtained. A sample was heated to constant weight at 180° and analyzed.

Subst., 0.3765; 0.1 *N* AgNO₃, 22.17 cc. Calc. for C₂₂H₁₂O₄Br₄: Br, 47.31; found: Br, 47.06.

This compound differs from the one previously described, and also from the one described by Meyer, in that it dissolves with difficulty in cold aqueous alkalis with a *pure blue* color, no violet being perceptible. On warming, more of the material goes into solution and the color becomes an intense pure blue; on cooling the color gradually fades, but does not become violet, and a white crystalline substance separates, presumably a salt of the tetrabromo- α -orcinolphthaleincarbinolcarboxylic acid (see pp. 1222 and 1227).

The tetrabromo compound is acted on by dry ammonia gas forming a very pale blue *di-ammonium* salt.¹

Subst. (dried at 140°), 0.6160; gain in weight: 0.0318. Calc. for C₂₂H₁₂O₄Br₄·2NH₃: 4.80; found: NH₃, 4.90.

The salt is unstable, however, and loses its ammonia very quickly in the air, more quickly indeed than is the case with the corresponding β -compound (see p. 1232).

Tetrabromo- α -orcinolphthalein Diacetate.—Five grams of tetrabromo- α -orcinolphthalein were boiled with 5 g. of sodium acetate and 50 cc. of acetic anhydride for one hour, and the mixture poured into a large volume of water. The slightly colored oil was allowed to solidify, filtered off, washed, dried, and dissolved in hot benzene. The solution was concentrated by distillation, and on cooling microscopic, irregular prisms separated. The colorless compound thus prepared melted at 297° with slight decomposition. Upon recrystallization from acetone the melting point was unchanged. A sample heated to constant weight at 180° was analyzed.

Subst., 0.5111; 0.1 *N* AgNO₃, 27.00 cc. Calc. for C₂₂H₁₀O₄Br₄(CH₃CO)₂: Br, 42.07; found: Br, 42.22.

Tetrabromo- α -orcinolphthalein diacetate is insoluble in water and in alkalis. It is soluble in hot benzene, difficultly soluble in hot acetone, and almost insoluble in methyl and in ethyl alcohol.

α -Orcinolphthalein Hydrochloride.—Five grams of pure α -phthalein were dissolved in 100 cc. of absolute alcohol, the solution cooled to 0° , and treated with dry hydrochloric acid gas for two hours. A small crop of dark reddish crystals separated, which increased considerably on allowing the solution to stand over night at 0° . The dark red product was filtered off and allowed to stand in the air till the odor of hydrochloric

¹ This work was done by Mr. J. J. Kennedy.

acid had disappeared. Examined under the microscope the material was seen to consist of well formed needles. A portion was finely ground and the loss on heating determined. The material lost weight slowly at 95° , more rapidly at 140° , finally coming to constant weight in three-quarters of an hour at 178° . It slowly became *colorless* as it lost weight.

Subst., 0.3055; loss, 0.0343. Calc. for $C_{22}H_{16}O_4 \cdot HCl$: HCl, 9.20; found: loss, 11.23.

The hydrochloric acid actually combined was determined by weighing a portion of the air-dried material into an Erlenmeyer flask, adding water and warming till the solution was decolorized, *i. e.*, the hydrochloride was completely decomposed. The insoluble phthalein was filtered off, washed and the free acid in the filtrate determined by titration with standard alkali using phenoltetrachlorophthalein as the indicator. From the above loss in weight the weight of the phthalein actually taken was calculated.

Hydrochloride, 0.6346; phthalein, 0.5633; HCl, 0.05762. Calc. for $C_{22}H_{16}O_4 \cdot HCl$: HCl, 9.20; found: HCl, 9.28.

Therefore, one molecule of α -orcinolphthalein combines with one molecule of hydrogen chloride. Probably a small amount of alcohol was present in this compound as indicated by the figure for the loss on heating. The hydrochloride is quite stable as shown by the fact that a fairly high temperature is required to drive off the hydrochloric acid.

Dry hydrochloric acid gas is without action on the α -phthalein, but when treated with fuming hydrochloric acid the *white* phthalein forms the dark red hydrochloride without dissolving in the acid.

Colorless Monopotassium Salt of α -Orcinolphthalein Carbinol Carboxylic Acid.

This salt was first prepared by A. von Baeyer (see p. 1208). According to him, it forms so readily that it may be employed as a means of separating the α - and β -isomers. The lactoid formula, which he gives to this salt to explain its lack of color, is very unusual and the compound was therefore again prepared and carefully studied.

Several preparations were made, of which the following may be taken as typical: Very pure α -phthalein, was dissolved in absolute ethyl alcohol. To this colorless solution half normal alcoholic potassium hydroxide was added slowly from a buret with constant shaking. A purplish red coloration appeared, which very quickly disappeared at first, but more slowly as the end point was approached, and meanwhile a white crystalline powder separated. The addition of alkali was discontinued before a permanent color was imparted to the solution. The potassium salt was then filtered off. It was pure white but on drying in the air for some time assumed a faint lavender tint. Dried for one-half hour at 120° in a current of hydrogen the material reached constant weight and became *markedly colored dark bluish wine-red* (it became brownish as a result of oxidation if not heated in an inert gas). The

hydrogen and escaping vapors were bubbled through cold water contained in a U-tube. The contents of this tube gave a faint but distinct test for alcohol. The loss in weight (I) is due to water and some alcohol. On standing in the air all the alcohol is lost and the loss in weight from the lavender compound corresponds to one molecule of water. On heating moisture collected on the cool part of the tube of the drying apparatus, and the water through which the escaping vapors were passed gave no test for alcohol (II).

Subst., (I) 0.2804, (II) 0.3731; loss, H_2O , (I) 0.0224, (II) 0.0166.

Calc. for $\text{C}_{22}\text{H}_{17}\text{O}_4\text{K} \cdot \text{H}_2\text{O}$: 4.33; found: H_2O , (I) 7.99, (II) 4.45.

Material dried for this short time is hygroscopic, and on *absorption of moisture becomes again nearly colorless*. If the dried red salt be heated for an hour and a half at 120° in a current of hydrogen it increases in weight a trifle over the weight obtained on heating for one-half hour at 120° , becomes slightly brownish, but is no longer hygroscopic, and does not lose its color on standing in the air for several days.

Potassium determinations were made in the following manner: a weighed amount of the dried sample was warmed in aqueous solution with an excess of 0.1 *N* hydrochloric acid until the salt was entirely decomposed. After filtering and washing the precipitated phthalein, the excess of acid remaining was determined by titration with standard alkali using phenol-tetrachlorophthalein as the indicator.

Subst., (I) 0.3532, (II) 0.3218; 0.1 *N* HCl, (I) 8.86, (II) 7.95 cc.

Calc. for $\text{C}_{22}\text{H}_{17}\text{O}_4\text{K}$: K, 9.82; found: K, (I) 9.81, (II) 9.66.

Another sample of the *freshly prepared* salt was analyzed by Mr. F. W. Sherwood.

Subst., (I) 0.3639, (II) 0.4805; loss at 160° , (I) 0.1005, (II) 0.1300. Calc. for loss of 3 $\text{C}_2\text{H}_5\text{OH}$ and 1 H_2O :¹ 28.16; found: (I) 27.62; (II) 27.06.

Both water and alcohol were given off and the salt became *colored red*. The residues were fumed down with sulfuric acid to determine the amount of potassium present.

Subst., (I) 0.2642, (II) 0.3481; K_2SO_4 , (I) 0.0556, (II) 0.0755.

Calc. for $\text{C}_{22}\text{H}_{17}\text{O}_4\text{K}$: K, 9.82; found: K, (I) 9.45, (II) 9.74.

This colorless monopotassium salt of α -orcinolphthaleincarbinolcarboxylic acid dissolves with difficulty in water, imparting a wine-red color to the solution. On boiling or on long standing this dilute solution becomes colorless, and a white precipitate separates, the lactoid form of the α -orcinolphthalein.

¹ Kober and Marshall, *THIS JOURNAL*, 34, 1424 (1912), have made colorless monopotassium and monosodium salts of phenolphthalein carbinolcarboxylic acid, and have found that, when made in alcoholic solutions, these salts contain both water and alcohol. In aqueous solutions these salts undergo hydrolysis and phenolphthalein precipitates exactly as this colorless salt of α -orcinolphthalein carbinolcarboxylic acid gives α -orcinolphthalein on hydrolysis.

Colored Monopotassium Salt of α -Orcinolpthalein.

Baeyer states that, if α -orcinolphthalein be boiled with soda solution, fine, hair-like needles of the violet disodium salt separate out on cooling. This product was not analyzed and it was therefore deemed necessary to repeat this work, and isolate and analyze the compound. Boiling α -phthalein with normal soda solution did give on cooling a crop of hair-like needles. Under the microscope these were seen to be quite well formed and appeared wine-red by transmitted light. They formed felt-like masses on the filter and packed together so tightly that they could not be sucked dry, and as they were unstable in the presence of water or of alcohol there seemed to be no method of completely removing the mother liquor. The potassium salt prepared in an analogous manner presented similar difficulties. It was finally obtained pure as follows: Five grams of potassium carbonate dissolved in 250 cc. of 50% alcohol, were heated to boiling, and an alcoholic solution of pure α -orcinolphthalein (5 g. in 50 cc.) was added through the reflux condenser. The solution became at once purplish red colored. It was allowed to stand forty eight hours, by which time crystals had formed which were filtered off. They appeared dark red in mass and under the microscope were seen to be long, purplish red needles, almost perfectly formed. They dissolved only partly in water, and imparted a wine red color to the solution. On drying in hydrogen a sample came to constant weight in one case, I, in one hour at 110° , and in another, II, in one-half hour at 120° .

Subst., (I) 0.1379, (II) 0.1551; loss, (I) 0.0080, (II) 0.0081.

Calc. for $C_{22}H_{18}O_4K.H_2O$: 4.33; found: H_2O , (I) 5.80, (II) 5.22.

Sample I had been allowed to dry in the air for a few hours before heating, while II had stood for four days. The dried anhydrous material showed no tendency to absorb moisture and become colorless as was the case with the colorless monopotassium salt (see p. 1223). A potassium determination was made in the same manner as in the case of the colorless monopotassium salt. A portion of the dried sample, I, was used.

Subst., 0.1294; 0.1 N HCl, 3.34 cc. Calc. for $C_{22}H_{18}O_4K$: K, 9.82; found K, 10.09.

The following analyses were made by Mr. F. W. Sherwood on a fresh preparation of this salt:

Subst., (I) 0.1738, (II) 0.2013; loss, (I) 0.0139, (II) 0.0160.

Calc. for $C_{22}H_{18}O_4K.2H_2O$: 8.30; found: H_2O (I) 8.00, (II) 7.95.

Subst., (I) 0.1600, (II) 0.1856; K_2SO_4 , (I) 0.0366, (II) 0.0422.

Calc. for $C_{22}H_{18}O_4K$: K, 9.82; found: K, (I) 10.27, (II) 10.20.

The substance is therefore a *mono*- and not a *di*-potassium salt as stated by Baeyer.

Professor Gill of the Department of Mineralogy and Crystallography of Cornell University has examined the crystals of this red monopotassium salt and reports as follows: "Elongated crystals or needles, which show

parallel extinction and are so frequently flattened as to indicate that they are probably not tetragonal or hexagonal. Long direction less elasticity, greater absorption. Pleochroism strong, from colorless or yellowish red to purple in very thin crystals; from red with brown-orange tinge to black in the stout needles. Stout crystals with six-sided cross section. Double refraction not strong, interference color obscured by absorption in thick crystals. Optical figure symmetrical, hence not monoclinic. Without much doubt orthorhombic, possibly hexagonal, as the plane of the optical axis seems parallel to the elongation. Good cross cleavage at right angles to the length."

If this monopotassium salt of α -orcinolphthalein be boiled with a large amount of water, the wine red solution becomes decolorized, and well formed *colorless* needles of the α -phthalein separate. The solution does not become colored on cooling. If a few drops of an alcoholic solution of phenoltetrachlorophthalein be added to this colorless supernatant liquid, a marked reddish coloration results, *i. e.*, free alkali is present. The phenomenon of decoloration is, therefore, one of hydrolysis, and is in accord with the statement of Baeyer (see p. 1208) in regard to the decomposition of the colorless salt in aqueous solution and also agrees with Meyer's statement (see p. 1205) in regard to the very weak acid nature of the α -phthalein.

The ease with which this potassium salt undergoes hydrolysis in aqueous solution also explains the fact, noted by Meyer, that the solution of the α -phthalein in *dilute* potassium hydroxide is decolorized by shaking with ether. The free phthalein is very soluble in ether, but insoluble in water, and, as fast as it is formed by the hydrolysis of the salt, it is removed by the ether until finally none is present in the alkaline solution, *i. e.*, the solution is decolorized.

Dipotassium Salt of α -Orcinolphthalein.

Baeyer states that if α -orcinolphthalein be boiled with concentrated potassium hydroxide the solution becomes pure blue, and crystals of the *tetrapotassium* salt separate. He believed that the formation of this salt was due to the rupture of the pyrone ring. Since the rupture of this ring is unusual, and takes place only in the case of the very acid phthaleins and since α -orcinolphthalein is a very weak acid, it was deemed necessary to repeat this work. Concentrated aqueous potassium hydroxide (1 : 1) gave a large crop of poorly crystallized material that could not be even approximately freed from its mother liquor. Analysis of this product gave over 30% potassium, the large amounts of potassium hydroxide and potassium carbonate present being indicated by slight white incrustations on the air-dried material. Anticipating this difficulty, a portion of the freshly prepared material was filtered separately, and washed several

times with absolute alcohol. The filtrate was strongly purplish red colored and the material on the filter analyzed as follows:

Subst., 0.2735, dried, 0.2654; 0.1 *N* HCl, 10.83 cc. Calc. for $C_{22}H_{14}O_4K_4$: K, 29.48. Calc. for $C_{22}H_{14}O_4K_3$: K, 17.92; found: K, 15.96.

The salt evidently breaks up in alcoholic solution, and the potassium hydroxide or potassium ethylate formed is washed out at a greater rate than is the free phthalein. A fairly pure salt was finally obtained as follows: seventy-five cc. of 1 : 1 potassium hydroxide were diluted to 150 cc. with water, heated to 85° and 5 g. of pure α -phthalein, dissolved in 100 cc. alcohol, added. The solution became violet, not blue colored, and on cooling two liquid layers formed. About 85 cc. of the alcohol and water were then distilled off, when the solution became pure blue and homogenous, and blue crystals having a bronzy luster began to separate from the hot solution. The whole was allowed to cool, whereupon the separation of the salt was nearly complete, and the mother liquor was no longer highly colored, due to the formation of the *tripotassium* salt of the carbinol acid (see p. 1227). The crystals were filtered off and dried in the air. In mass they appeared blue with a decided bronzy luster. Under the microscope they appeared pure blue. They dissolved in water almost completely at once and imparted a purplish red color to the solution. On heating in hydrogen the crystalline material came to constant weight in one-half hour at 110°.

Subst., (I) 0.4895, (II) 0.4141; loss, (I) 0.0233, (II) 0.0163.

Calc. for $C_{22}H_{14}O_4K_3 \cdot H_2O$: 3.97; found: H_2O , (I) 4.76, (II) 3.94.

Sample I had been allowed to dry over night in the air, while Sample II had stood in the air for ten days.

Potassium was determined in the same manner as in the case of the monopotassium salts.

Subst., (I) 0.4653, (II) 0.3969; 0.1 *N* HCl, (I) 21.91, (II) 19.00 cc. Calc. for $C_{22}H_{14}O_4K_4$: K, 29.48; calc. for $C_{22}H_{14}O_4K_3$: K, 17.92; found: K, (I) 18.41, (II) 18.72.

The salt is therefore a *di*- and not a *tetrapotassium* salt as stated by Baeyer (see p. 1210).

This blue dipotassium salt was obtained beautifully crystallized by dissolving 2.5 g. of the *pure* α -phthalein diacetate in 900 cc. of hot alcohol and pouring this solution into a boiling solution of 7.5 g. of potassium hydroxide in 100 cc. of alcohol. After boiling for a short time one-half of the alcohol was distilled off and the solution allowed to stand over night. The crystals were then filtered off, dried in the air, and analyzed.¹

Subst., (I) 0.3436, (II) 0.3352; loss at 110°, (I) 0.0114, (II) 0.0111. Calc. for $C_{22}H_{14}O_4K_2 \cdot H_2O$: 3.97; found: H_2O , (I) 3.32, (II) 3.31.

This salt contained no alcohol, the loss being due entirely to water.

Subst., (dried) (I) 0.2925, (II) 0.2877, (III) 0.1408; cc. 0.1 *N* HCl, (I) 13.96, (II) 13.47, (III) 6.55. Calc. for $C_{22}H_{14}O_4K_2$: K, 17.92; found: K, (I) 18.66, (II) 18.31, (III) 18.19.

¹ This salt was made and analyzed by Mr. F. W. Sherwood.

Professor Gill has examined the crystals of this *blue* dipotassium salt and reports as follows: "The substance is thoroughly crystalline, though not in good single crystals but in rosette-like groups of somewhat thick plates. These groups reach about $\frac{1}{2}$ mm. in diameter, and are composed of many sub-parallel individuals. There seem to be no impurities present in any appreciable quantity. The fact that extinction is in some positions parallel and in others as high as 15° or even 20° would suggest monoclinic crystallization. The surface color is a brilliant yellowish or greenish bronze. In very thin crystals the marked pleochroism is from dark purplish blue to a lighter clear blue, while thicker individuals change from black to dark blue when rotated above a nicol prism. Not enough light is transmitted to enable observation of the figure in converging polarized light." This dipotassium salt of the α -phthalein behaves, on boiling, in dilute aqueous solutions just as do the two monopotassium salts, although, of course, a proportionately larger amount of water is required to produce complete decoloration.

Tripotassium Salt of α -Orcinolpthalein Carbinol Carboxylic Acid.

This salt was obtained from the mother liquor from which the dipotassium salt had crystallized out (see p. 1226). In mass the salt appeared *pale blue* to the naked eye, but under the microscope it could be seen to consist of almost *colorless needles* mixed with some crystals of the *blue* dipotassium salt. After being dried at 155° in hydrogen the material gave results on analysis agreeing with those required for the tripotassium salt of the carbinol carboxylic acid.¹

Subst., (I) 0.3216, (II) 0.4053; loss, (I) 0.0284, (II) 0.0347. Calc. for $C_{22}H_{11}O_6K_3 \cdot 2.5H_2O$: 3.38; found: (I) 8.83, (II) 8.56. Subst., (dried) (I) 0.3584, (II) 0.2968; K_2SO_4 , (I) 0.1880, (II) 0.1537. Calc. for $C_{22}H_{11}O_6K_3$: K, 23.82; found: K, (I) 23.54, (II) 23.24.

This salt undergoes hydrolysis when boiled with water, exactly as the other potassium salts of the α -phthalein do. Kober and Marshall² have made a *tripotassium* salt of phenolphthalein carbinolcarboxylic acid which hydrolyzes with water in the same manner that this salt does.

It is highly probable that this is the salt analyzed by Baeyer and which he called a *tetrapotassium* salt (see p. 1210).

β -Orcinolpthalein.

β -Orcinolpthalein was obtained free from its isomers as outlined above (see p. 1217). The last traces of the γ -compound were removed by the ammonia method of Kehrman. In order to insure the complete removal of the α -isomer from the soda solution it is necessary to use *two* portions of ether, and also to take care that the concentration of the α -phthalein

¹ These analyses were made by Mr. F. W. Sherwood.

² THIS JOURNAL, 33, 1780 (1911).

in the smaller portions of ether does not become sufficiently great to permit this compound to pass into the soda solution.

The crude β -orcinolphthalein was crystallized first from methyl alcohol, then from methyl alcohol by the addition of water, and finally from ethyl alcohol by the addition of water. From the last two solutions a mixture of colorless and colored needles were obtained when the water was added to the *hot* solutions. Perfectly white needles were obtained by the addition of cold water to the solution in methyl alcohol surrounded by ice. This product was filtered off, allowed to dry in the air, and the loss on heating determined. The material came to constant weight in one hour at 120° *without becoming colored*, but on further heating for one-half hour at 185° it was converted into the stable *yellow quinoid form without change of weight*. The following determinations show that the product crystallized from methyl alcohol by the addition of water contains a molecule of methyl alcohol (I), or is a mixture of this compound with the hydrate (II), (III).

Subst., (I) 0.3640, (II) 0.5611, (III) 0.1655; loss, (I) 0.0336, (II) 0.0369, (III) 0.0117. Calc. for $C_{22}H_{16}O_6 \cdot CH_3OH$: 8.17; for $C_{22}H_{16}O_6 \cdot H_2O$: 4.76; found: (I) 9.23, (II) 6.58, (III) 7.07.

The yellow material obtained in determination (I) was shown to be the anhydrous β -orcinolphthalein (see p. 1206) by the following analysis:

Subst., 0.0920; CO_2 , 0.2482; H_2O , 0.0358. Calc. for $C_{22}H_{16}O_6$: C, 73.31; H, 4.48; found: C, 73.58; H, 4.36.

The colored quinoid form of the β -orcinolphthalein was obtained crystalline in the following manner: a few grams of the material, shown to be pure by the above analysis, were dissolved in boiling alcohol, an equal volume of hot water added and the boiling continued. Yellow crystals separated, which consisted of minute, well formed, six-sided plates. The air-dried material lost only 0.1% of its weight on heating for one-half hour at 185° . From the filtrate there separated on cooling a mixture of the colored and colorless forms consisting of plates and needles, respectively. The yellow quinoid form of the β -orcinolphthalein may also be obtained crystalline from glacial acetic acid (see p. 1230).

β -Orcinolphthalein dissolves in ammonia, caustic alkalis, and in alkali carbonates with an intense cherry-red color. It does not, however, dissolve appreciably in cold ammonium carbonate, or in cold sodium bicarbonate solutions. It dissolves in alcoholic ammonia with a *red* color. When this solution is treated with water it turns *blood red*. When perfectly pure, and when none of the γ -phthalein is present, the solution in alcoholic ammonia shows no trace of the *greenish fluorescence* so characteristic of the γ -phthalein (see p. 1234). Dry ammonia gas does not act upon the *quinoid* form of the phthalein provided it be *perfectly pure*. Curiously enough, however, the *dry lactoid* modification absorbs nearly a molecule of dry ammonia gas (found 4.07 and 3.92% NH_3 , calculated

for one molecule of ammonia, 4.51%) without becoming colored. This colorless compound with ammonia loses all the ammonia when heated to 130°. When allowed to stand in the air for several weeks it loses all its ammonia and takes up moisture to form the colorless hydrate (see below).

β -Orcinolpthalein is precipitated from alkaline solutions by acetic acid as white flocks and by mineral acids as yellow flocks. The latter slowly become white on standing or at once if the mixture be heated. Kehrman (see p. 1211) regarded this color change as one from the quinoid form of the free β -phthalein to the stable lactoid form. This is, however, incorrect, the *yellow quinoid* form being, as shown above, the *stable* one, while the *white* product is a mixture of the *unstable lactoid* and *lactoid hydrate* forms (see p. 1230). The yellow compound obtained on precipitation with mineral acids contains a small amount of the *colored* quinoid sulfate or hydrochloride, which slowly hydrolyzes in the cold, or rapidly on heating, to the colorless phthalein and its hydrate. Acetic acid does not form a salt with the phthalein, therefore it precipitates the phthalein as the *white* hydrate, which goes over to the *colored* anhydrous form on boiling (see p. 1230).

β -Orcinolpthalein Hydrate.— β -Phthalein was dissolved in dilute alkali and poured into dilute acetic acid. A white, flocculent precipitate separated, a portion of which was filtered off, washed, dried in the air, and the loss on heating determined. The material came to constant weight in one-half hour at 150°, and did not change color, but on heating for one-half hour at 185° it became *colored yellow without change of weight*.

Subst., (I) 0.2653, (II) 0.1941, (III) 0.4659; loss, (I) 0.0140, (II) 0.0100, (III) 0.0244. Calc. for $C_{22}H_{16}O_6 \cdot H_2O$: 4.76; found: H_2O , (I) 5.28, (II) 5.15, (III) 5.24.

This material had been dried in the air for two weeks. It probably contains a small amount of acetic acid (see p. 1231). Another portion of the above suspension of freshly precipitated hydrate was boiled for one hour, which caused it to change slowly from the *colorless* hydrate to the yellow phthalein. This product lost only 1.16% on heating for one-half hour at 150°. It is therefore the anhydrous quinoid form, containing a very small amount of the hydrate. This transformation was no doubt due to the solvent action which the small excess of acetic acid had on the hydrate, thus lowering decidedly the temperature of transition into the stable quinoid form. Such a transformation by partial solution is also illustrated by the following experiment. Some of the colorless air-dried hydrate was boiled in benzene for thirty minutes. It was converted into the yellow phthalein, which lost only 0.63% on heating.

That the product obtained on heating was really the anhydrous β -orcinolphthalein is shown by the following analysis:

Subst., 0.1349; CO_2 , 0.3611; H_2O , 0.0558. Calc. for $\text{C}_{22}\text{H}_{10}\text{O}_5$: C, 73.31; H, 4.48; found: C, 73.00; H, 4.63.

If the β -orcinolphthalein be precipitated from alkaline solution by mineral acids it separates as a mixture of the lactoid phthalein and its colorless hydrate:

Subst., (I) 0.4246, (II) 0.2863, (III) 0.1898; loss, H_2O , (I) 0.0112, (II) 0.0070, (III) 0.0040. Calc. for $\text{C}_{22}\text{H}_{10}\text{O}_5 \cdot \frac{1}{2}\text{H}_2\text{O}$: 2.44; found: H_2O , (I) 2.64, (II) 2.45, (III) 2.11.

The yellow product which at first separates is completely hydrolyzed during the subsequent filtering and washing, so that the final product is perfectly white. It becomes white at once on heating the mixture, but is not further transformed into the stable quinoid form.

Behavior of β -Orcinolphthalein toward Glacial Acetic Acid.—Inasmuch as E. Fischer believed that orcinolphthalein formed a monoacetyl derivative (see p. 1202) on heating with glacial acetic acid, and further since Meyer considered this monoacetyl derivative of E. Fischer to be identical with his β -orcinolphthalein (see p. 1206), because the combustion analyses and certain properties of E. Fischer's product agreed with those of his β -orcinolphthalein, the behavior of the *pure* β -phthalein toward glacial acetic acid was carefully studied.

Some of the white β -orcinolphthalein hydrate was boiled with glacial acetic acid for some time. Only partial solution took place and the insoluble material assumed a yellow color. This material was filtered off. From the hot filtrate there separated on cooling a small crop of *yellow plates* exactly similar to those obtained from *hot* alcohol (see p. 1228). The yellow substance, *which did not dissolve in the acetic acid*, was examined under the microscope and seen to consist of needles. This material was finely ground, allowed to stand in the air until all odor of acetic acid had disappeared, and the loss in weight on heating to 125° determined.

Subst., 0.3164; loss, 0.0009 g.; loss, 0.28%.

That this dried material is the anhydrous phthalein is shown by the following analysis:

Subst., 0.1122; CO_2 , 0.3015; H_2O , 0.0457. Calc. for $\text{C}_{22}\text{H}_{10}\text{O}_5$: C, 73.31; H, 4.48; found: C, 73.29; H, 4.56.

The material which separated from the *hot* filtrate in yellow plates was filtered off, dried, and analyzed. It came to constant weight in one-half hour at 190° .

Subst., 0.2351; loss, 0.0024 g.; loss, 1.02%.

The material thus dried was shown to be the anhydrous phthalein by the following analysis:

Subst., 0.0969; CO_2 , 0.2599; H_2O , 0.0393. Calc. for $\text{C}_{22}\text{H}_{10}\text{O}_5$: C, 73.31; H, 4.48; found: C, 73.15; H, 4.54.

The results show that Emil Fischer's monoacetyl orcinolphthalein was

probably β -orcinolphthalein containing a small amount of acetic acid (see pp. 1202 and below).

Compound of β -Orcinolpthalein with Acetic Acid.—From the cold mother liquor obtained in the preceding preparation there separated on *long standing* a small amount of perfectly white microcrystalline powder. This was filtered off, dried in the air, finely ground, and allowed to stand till the odor of acetic acid had entirely disappeared. Heated in the drying apparatus it lost considerable weight at 115° , but at the end of an hour and a half it had not come to constant weight, so the temperature was increased to 180° . In one hour it had reached constant weight, but was only slightly yellow. It assumed the *yellow* color of the quinoid β -phthalein on heating for one-half hour longer.

Subst., 0.3793; loss, 0.0569. Calc. for $C_{22}H_{16}O_6 \cdot CH_3COOH$: 14.29; found: loss, 15.00

A sample was weighed into an Erlenmeyer flask, heated with water and the filtrate from this titrated, using phenoltetrachlorophthalein as the indicator.

Subst., 0.6238; 0.1 *N* NaOH, 15.14 cc. Calc. for $C_{22}H_{16}O_6 \cdot CH_3COOH$: 14.29; found: 14.57.

The yellow material which remained after heating at 180° was pure β -phthalein.

Subst., 0.1182; CO_2 , 0.3173; H_2O , 0.0466. Calc. for $C_{22}H_{16}O_6$: C, 73.31; H, 4.48; found: C, 73.21; H, 4.41.

β -Orcinolpthalein Diacetate.— β -Orcinolpthalein, free from its isomers and from tar, was converted into the acetate (see p. 1219), and this dissolved in hot benzene. On cooling clusters of *pure white* needles separated having a melting point of $226-227^{\circ}$. The melting point remained the same when the substance was recrystallized from absolute alcohol or from ethyl acetate. For the analysis it was heated to constant weight for one-half hour at 180° .

Subst., (I) 0.1754, (II) 0.1020; CO_2 , (I) 0.4527, (II) 0.2625; H_2O , (I) 0.0732, (II) 0.0440. Calc. for $C_{22}H_{16}O_6(CH_3CO)_2$: C, 70.25; H, 4.54; found: C, (I) 70.39, (II) 70.19; H, (I) 4.67, (II) 4.83.

β -Orcinolpthalein diacetate is insoluble in water, and in the alkalis, but is easily saponified by heating in the latter. It is quite readily soluble in hot benzene, slightly less so in hot absolute alcohol. It is rather easily soluble in acetone. It corresponds closely in its properties to the compound prepared by Meyer except that he reports it as being slightly colored.

β -Orcinolpthalein Dibenzoate.—Attempts to prepare this compound by boiling the β -phthalein with benzoyl chloride gave a product insoluble in alkalis, but which contained tar that was not easily removed by crystallization. It was then prepared by the Schotten-Baumann reaction (see p. 1219), boiled with alcohol, and the white residue crystallized from benzene.

Fine, white needles were obtained which melted at $234-235^{\circ}$. When recrystallized from benzene by the addition of absolute alcohol, or from alcohol they melted at $235-236^{\circ}$. The melting point given by Meyer for this compound, $244-245^{\circ}$, is certainly incorrect. For analysis the compound was dried at 195° .

Subst., 0.1342; CO_2 , 0.3741; H_2O , 0.0535. Calc. for $\text{C}_{22}\text{H}_{14}\text{O}_6$ ($\text{C}_6\text{H}_5\text{CO}$)₂: C, 76.03; H, 4.26; found: C, 76.03; H, 4.46.

β -Orcinolphthalein dibenzoate is insoluble in water, and in alkalis, and saponifies somewhat slowly with alkali. It is easily soluble in hot benzene, rather difficultly soluble in hot alcohol, difficultly in ethyl acetate.

Tetrabromo- β -orcinolphthalein was made from 20 g. of pure β -orcinolphthalein by the method given for the corresponding α -compound (see p. 1220). It weighed 35 g. which corresponds to 94.8% of the theory. Ten grams of this material were used for conversion into the diacetate, while the remainder was dissolved in cold alkali, filtered, and precipitated by pouring into dilute acid. It separated in white, gelatinous flocks, which after filtering and washing were extracted with three portions of alcohol, whereby a white amorphous powder was left. This gave the following result on analysis:

Subst., 0.5355; 0.1 N AgNO_3 , 31.68 cc. Calc. for $\text{C}_{22}\text{H}_{12}\text{O}_6\text{Br}_4$: Br, 47.31; found: Br, 47.28.

This tetrabromo- β -orcinolphthalein corresponds, in the main, to the compound prepared by Meyer. It is practically insoluble in all ordinary solvents; it dissolves in alkalis with a peculiar dirty dark reddish brown color, which in large volumes appears almost black by reflected light, but appears a dirty red by transmitted light.

Action of Dry Ammonia on Tetrabromo- β -orcinolphthalein.—Gaseous ammonia dried by passing through soda-lime, and then through a tube containing sodium wire was allowed to act on a weighed amount of tetrabromo- β -orcinolphthalein dried at 185° . The ammonia acted at once on the phthalein as indicated by the marked color, although eight hours were required to reach constant weight. The salt is almost black and is unstable. For this reason it must be placed in a tightly stoppered weighing tube when removed from the apparatus and weighed at once. On standing in the open air approximately half the ammonia was lost in three-quarters of an hour, and practically all of it had disappeared at the end of two days.

Subst., 0.3847; gain, 0.0360. Calc. for $\text{C}_{22}\text{H}_{12}\text{O}_6\text{Br}_4 \cdot 3\text{NH}:\text{NH}_3$, 7.03; for $\text{C}_{22}\text{H}_{12}\text{O}_6\text{Br}_4 \cdot 4\text{NH}_3$: 9.16; found: NH_3 , 8.56.

The statement of Meyer¹ that "Ammoniakdämpfe wirken nicht auf ihn ein, sodass er sich leicht aus einen Gemenge von Tetrabrom- β - und γ -orcinolphthalein isoliren lässt," is therefore incorrect.

¹ Ber., 29, 2637 (1896).

Tetrabromo- β -orcinolphthalein Diacetate.—Ten grams of the tetrabromo- β -phthalein were converted into the acetate (see p. 1221). The crude product dissolved in hot benzene and crystallized by the addition of alcohol gave white needles which melted at 265–266°. Recrystallized from ethyl acetate they melted at 266–267°. A sample was dried at 180° for one-half hour and analyzed.

Subst., 0.3897; 0.1 *N* AgNO₃, 20.50 cc. Calc. for C₂₂H₁₀O₆Br₄(CH₃CO)₂: Br, 42.07; found: Br, 42.04.

Tetrabromo- β -orcinolphthalein diacetate is insoluble in alkalis; it is less readily saponified by aqueous alkali than the β -orcinolphthalein diacetate. It is quite soluble in hot benzene, rather difficultly soluble in hot ethyl acetate, and almost insoluble in hot absolute alcohol.

β -Orcinolphthalein Hydrochloride was made by the method given for the α -compound (p. 1221). The product was bright red, and under the microscope appeared as almost perfectly formed diamond-shaped plates. A small portion was finely ground and the loss on heating determined. It lost weight very slowly at 140°, but came to constant weight in one and one-half hours at 175°, gradually changing from *red* to *yellow*.

Subst., 0.3408; loss, 0.0415. Calc. for C₂₂H₁₀O₆.HCl: HCl, 9.20; found: loss, 12.18.

The amount of hydrochloric acid combined was determined by titration as in the case of the α -compound.

Subst., 0.5564; phthalein, 0.4887; HCl, 0.0499. Calc. for C₂₂H₁₀O₆.HCl: HCl, 9.20; found: HCl, 9.26.

Hence, one molecule of the phthalein combines with one molecule of hydrochloric acid. The difference between the figures obtained for the loss on heating and the hydrochloric acid actually present is probably due to a small amount of alcohol. Dry hydrochloric acid gas is without action on the β -phthalein, but the scarlet red hydrochloride is formed at once when it is treated with fuming hydrochloric acid.

γ -Orcinolphthalein.

γ -Orcinolphthalein was separated from the crude material by the method outlined above (see p. 1217). It may also be extracted from the crude product with a 10% solution of sodium bicarbonate. This dissolved the γ -isomer very slowly, however. Ammonium carbonate is a little more rapid, but has the disadvantage that traces of the β -compound are removed by it. The hydrochloric acid method of purifying the crude γ -compound proposed by Kehrmann (see p. 1211) was used in order to insure an absolutely pure product for this work. The solution in methyl alcohol was cooled to 0°, and treated with hydrochloric acid gas. The yellow-brown hydrochloride, which separated in rather poorly formed needles, was dissolved in alkali, the phthaleins precipitated with dilute acetic acid, washed and dried. This *bright yellow* material was then crystallized from

methyl alcohol and again converted into the hydrochloride, which now separated as clear yellow, almost perfectly formed needles. When this salt was dissolved in alkali, and the solution poured into dilute acetic acid the hydrate of the pure phthalein separated as *white* flocks (see p. 1235). In this manner a product is obtained which is absolutely free from tar (which apparently adheres more tenaciously to this isomer than to the others) and is also free from the isomeric phthaleins.

The γ -orcinolphthalein thus purified dissolves in alkalies with a clear yellow color, showing only a faint fluorescence, whereas the crude material exhibited a marked fluorescence. In both cases the fluorescence is very much increased by the addition of alcohol. Thicker layers of the more concentrated alkaline solutions show a slightly reddish brown color. When an alkaline solution of this *carefully purified* phthalein is poured into dilute acetic acid a *white* flocculent precipitate of the hydrate is formed (see p. 1235), whereas if not pure it gives a *yellow* precipitate. The hydrate made from *pure* material becomes beautifully crystallized on boiling for a short time with water (see p. 1236), being converted into the *yellow* anhydrous phthalein.

Pure γ -orcinolphthalein has remarkably little color in alkaline solutions as compared with the α - and β -isomers. For this reason, and because of the slight fluorescence in dilute alkaline solutions, the compound was not recognized as a phthalein until an analysis had been made. It is quite probable that the γ -phthalein in alkaline solutions exists largely in the form of salts of the carbinol acid. Towards *concentrated* alkalies it conducts itself exactly as fluorescein¹ does. If a small stick of solid caustic potash be added to an alkaline solution of the phthalein and the solution be boiled, the color changes from red to bluish green. On dilution this color changes back to red and, on standing or warming, to yellow with a greenish fluorescence which shows more distinctly on the addition of alcohol.

γ -Orcinolphthalein dissolves in ammonium and alkali carbonates and bicarbonates with the evolution of carbon dioxide. It dissolves quite slowly in ammonium carbonate, and in sodium and ammonium bicarbonate solutions. In alcoholic ammonia it dissolves with a *red* color and strong *greenish fluorescence*. When diluted with water this solution turns yellow and the greenish fluorescence becomes less marked. It crystallizes well out of methyl or ethyl alcohol, and acetic acid, or by the addition of water to any of these solutions.

Compound of γ -Orcinolphthalein with Ethyl Alcohol.—Some of the pure material was dissolved in ethyl alcohol, the solution cooled, and crystallization caused to take place by the addition of water. The material separated as colorless plates, which on heating at 110° for two hours

¹ See *Ann.*, 372, 108 (1910).

came to constant weight and became *bright golden yellow*. When heated to 185° it became *grayish white* without further loss of weight.

Subst., 0.3074; loss, 0.0352. Calc. for $C_{22}H_{16}O_6 \cdot C_2H_5OH$: C_2H_5OH , 11.34; found: C_2H_5OH , 11.45.

This loss was due entirely to alcohol; no moisture condensed on the tube.

γ -Orcinolphthalein therefore crystallizes with a molecule of ethyl alcohol. That the above material is the pure phthalein is shown by the following analysis:

Subst., 0.1139; CO_2 , 0.3078; H_2O , 0.0497. Calc. for $C_{22}H_{16}O_6$: C, 73.31; H, 4.48; found: C, 73.70; H, 4.88.

The *dark orange* colored product observed by R. and H. Meyer (see p. 1207) was obtained in this work only in the case of *impure material*. Crude γ -phthalein which had been obtained from the unpurified mixture was crystallized from glacial acetic acid, whereby *dark orange* colored, rather poorly formed crystals separated. This product after drying in the air, when heated to 175° in the drying apparatus lost weight and fused to a dark, plastic mass which on cooling became hard and brittle, i. e., contained tar. The carefully purified γ -phthalein when crystallized from glacial acetic acid is *yellow*; the *dark orange* colored product observed by Meyer and also in this work is therefore impure.

Compound of γ -Orcinolphthalein with Methyl Alcohol.—If a saturated solution of pure γ -phthalein in methyl alcohol be allowed to stand, colorless cubical crystals separate. These lose weight very slowly at 110° , rapidly at 160° , coming to constant weight in one-half hour. They change to a bright yellow color as they lose weight and on heating to 185° or 190° for one-half hour longer they change to a grayish white.

Subst., (I) 0.9046, (II) 0.5225, (IIa) 0.3824, (IIb) 0.3481; loss, (I) 0.0762, (II) 0.0434, (IIa) 0.0316, (IIb) 0.0288.

Calc. for $C_{22}H_{16}O_6 \cdot CH_3OH$: CH_3OH , 8.17; found: CH_3OH , (I) 8.42, (II) 8.31, (IIa) 8.26, (IIb) 8.27.

Determinations I and II were made on material crystallized from pure methyl alcohol, (IIa) and (IIb) on the white needles obtained by the addition of water to the mother liquor from which the material used in determination II had separated. The loss was entirely due to alcohol as no moisture condensed on the tube.

γ -Orcinolphthalein Hydrate.—A few grams of *pure* γ -phthalein were dissolved in sodium carbonate solution, and poured into dilute acetic acid. The *white* flocculent precipitate was filtered off, washed, dried in the air, and the loss on heating determined. All the water was given off in two hours at 70° , and moisture condensed on the cool part of the drying tube. The material gradually changed to a *bright yellow* as it lost water. It lost no further weight on being heated for one-half hour at 180° .

Subst., (I) 0.2472, (II) 0.2448, (III) 0.1907, (IV) 0.2304; loss, (I) 0.0123, (II) 0.0116, (III) 0.0093, (IV) 0.113.

Calc. for $C_{22}H_{16}O_6 \cdot H_2O$: H_2O , 4.76; found: H_2O , (I) 4.98, (II) 4.74, (III) 4.88, (IV) 4.90.

These determinations were made on three different preparations: (I), (II) and (III) were on material that had dried in the air from five to seven days, while (IV) was on material that had stood in the air for *five weeks*.

When the hydrate is boiled with water it is converted into anhydrous γ -phthalein. A portion of the above prepared hydrate was boiled with water for two hours, at the end of which time it had become *yellow* and beautifully crystallized in rhomboidal plates. This material lost only 0.01% of its weight on heating to 180° for half an hour, *i. e.*, it is the anhydrous phthalein. Another preparation of the hydrate lost 4.53% water and became *bright yellow* when kept in a Hempel vacuum desiccator for 24 hrs. with sulfuric acid.

γ -Orcinolphthalein Diacetate.— γ -Phthalein was converted into its diacetyl derivative in the same manner as in the case of the α -isomer (see p. 1219). The colorless crude product was crystallized from benzene. Perfectly white needles were obtained which melted sharply at $206-207^\circ$. When recrystallized from absolute alcohol, and then from ethyl acetate, the melting point of the substance remained the same. For analysis a sample was dried for three-quarters of an hour at 195° .

Subst., 0.1470; CO_2 , 0.3782; H_2O , 0.0613. Calc. for $C_{22}H_{14}O_6(CH_3CO)_2$: C, 70.25; H, 4.54; found: C, 70.17; H, 4.67.

The diacetate corresponds exactly to the compound prepared by Meyer. It is insoluble in water and in alkalis and is easily saponified by the latter, especially if alcohol be added. It is soluble in benzene, hot absolute alcohol, and hot ethyl acetate, and crystallizes from any of these solutions.

γ -Orcinolphthalein dibenzoate was made by the method used in making the α -isomer (see p. 1219). After filtering off the slightly orange-colored product, it was triturated with alkali, washed with water, boiled with alcohol and crystallized from benzene by the addition of absolute alcohol. Pure white needles were obtained which melted at $284-285^\circ$, with slight carbonization. When recrystallized from acetone its melting point was unchanged. For analysis the material was dried for one-half hour at 190° .

Subst., 0.0825; CO_2 , 0.2300; H_2O , 0.0334. Calc. for $C_{22}H_{14}O_6(C_6H_5CO)_2$: C, 76.03; H, 4.26; found: C, 76.04; H, 4.53.

The dibenzoate is insoluble in alkalis, and is saponified rather slowly by these solutions. It is easily soluble in benzene, and rather difficultly soluble in hot acetone. It is almost insoluble in methyl and ethyl alcohols and in ethyl acetate.

Tetrabromo- γ -orcinolphthalein was made in the same manner as the

α -isomer (see p. 1220), dissolved in alkali, and precipitated by pouring into dilute acid. The orange-colored flocks were filtered off, washed, and then boiled with alcohol, this treatment changing the product to a colorless form. For analysis it was heated for half an hour to 175° .

Subst., 0.4616; 0.1 N $AgNO_3$, 27.27 cc. Calc. for $C_{22}H_{12}O_8Br_4$: Br, 47.31; found: Br, 47.22.

Tetrabromo- γ -orcinolphthalein corresponds closely with the compound prepared by Meyer. It shows the greatest analogy to eosin of any of the tetrabromoorcinolphthaleins, dissolving in alkalis with a rose-red color. It is a good dye and is almost insoluble in all the ordinary solvents.

Tetrabromo- γ -orcinolphthalein diacetate was made by the method used in preparing the α -isomer (see p. 1221). The crude product was crystallized from ethyl acetate. In the melting point tube it became pink above 240° ; this color disappeared above 270° , and the slightly darkened material melted quite sharply at $282-283^{\circ}$, and carbonized at a slightly higher temperature. When recrystallized from absolute alcohol it was obtained as perfectly white, well formed rhomboidal plates. These behaved in a melting point tube exactly as did the above material, and also melted at $282-283^{\circ}$. Bromine determinations were made on the material dried at 180° for one-half hour.

Subst., (I) 0.3358; (II) 0.5090; 0.1 N $AgNO_3$, (I) 17.35, (II) 26.25 cc. Calc. for $C_{22}H_{10}O_8Br_4(CH_3CO)_2$: Br, 42.07; found: Br, (I) 41.30; (II) 41.23.

The only explanation of the low percentage of bromine that suggests itself is that during the acetylation a small amount of bromine was eliminated by the action of the sodium acetate, since the tetrabromo compound from which the diacetate was made gave results on analysis for bromine agreeing with the theory (see above).

The diacetate is soluble in hot benzene, moderately in hot ethyl acetate, and quite difficultly soluble in hot absolute alcohol. It is insoluble in water and in alkalis, and is saponified rather difficultly by aqueous solution of the alkalis.

Action of Dry Ammonia Gas on γ -Orcinolphthalein.

Diammonium Salt of γ -Orcinolphthalein.—That γ -orcinolphthalein is more acid than its isomers is shown by the fact that it is acted upon so readily by dry ammonia gas. When the pure dry γ -phthalein was placed in a current of dry ammonia gas it gained weight rapidly, changed color (yellow to orange) and came to constant weight in 17 minutes. The boat containing the material was placed at once in a tightly stoppered tube and weighed. The gain in weight corresponds to two molecules of ammonia. The salt formed is unstable, however, and loses its ammonia rapidly on standing in the air.

Subst., 0.3871; gain, (NH_3) , 0.0377. Calc. for $C_{22}H_{14}O_8(NH_4)_2$: NH_3 , 8.64; found: NH_3 , 8.87.

Fluorescein and tetrachlorofluorescein¹ conduct themselves towards dry ammonia gas in the same manner as the γ -phthalein, thus showing the close resemblance of the γ -phthalein to fluorescein. The γ -phthalein is the only one of the isomers which forms a *salt* with ammonia gas.

Action of Dry Ammonia Gas on the Anhydrous Tetrabromo- γ -orcinolphthalein.—Dry ammonia gas was allowed to act on the anhydrous tetrabromo- γ -orcinolphthalein. It became pink at once, changed in a short time to a bright red, and at the end of three hours had become dark red. Approximately four molecules of ammonia are absorbed. The compound thus formed is unstable, giving up its ammonia slowly on standing in the air.

Subst., 0.5677; gain, (NH_3) , 0.0551. Calc. for $\text{C}_{22}\text{H}_{12}\text{O}_8\text{Br}_4 \cdot 3\text{NH}_3$: NH_3 , 7.03. Calc. for $\text{C}_{22}\text{H}_{12}\text{O}_8\text{Br}_4 \cdot 4\text{NH}_3$: NH_3 , 9.16; found: NH_3 , 8.85.

Tetrachloroeosin combines with *five* molecules of ammonia.²

γ -Orcinolphthalein Hydrochloride.—A portion of the γ -phthalein hydrochloride, purified as described above (see p. 1233), was dried in the air, ground, and the loss on heating determined. The compound is quite stable, losing weight slowly at 140° , and coming to constant weight only after four and one-half hours heating at 175° .

Subst., 0.4373; loss, 0.0502. Calc. for $\text{C}_{22}\text{H}_{16}\text{O}_8 \cdot \text{HCl}$: HCl, 9.20; found: loss, 11.48.

The amount of hydrochloric acid actually present was determined by titration in the same manner as in the case of the isomeric compounds (see pp. 1221 and 1233).

Hydrochloride, 0.3287; phthalein, 0.2910; HCl, 0.02891. Calc. for $\text{C}_{22}\text{H}_{16}\text{O}_8 \cdot \text{HCl}$: HCl, 9.20; found: HCl, 9.04.

The difference between the loss on heating and the amount of hydrochloric acid actually present is due to the presence of a small amount of alcohol.

Dry hydrochloric acid gas acts on the anhydrous γ -phthalein, one molecule of the acid being taken up with but little change in color. When heated to 180° the hydrochloride loses all its hydrochloric acid and gives the original weight of the γ -phthalein. The material thus obtained, when placed in a current of dry hydrochloric acid gas, again absorbs an equivalent of one molecule of hydrochloric acid, coming to constant weight in an hour and a half. The original weight of the γ -phthalein was obtained a second time by heating the hydrochloride to 180° .

Subst., (I) 0.4472, (II) 0.4472; gain in wt., (I) 0.0494, (II) 0.0452. Calc. for $\text{C}_{22}\text{H}_{16}\text{O}_8 \cdot \text{HCl}$: HCl, 9.20; found: HCl, (I) 9.95, (II) 9.18.

In (I) the boat containing the material was quickly transferred to a tightly stoppered tube, and weighed at once. In (II) the material was

¹ THIS JOURNAL, 36, 690 (1914).

² *Ibid.*, 36, 706 (1914).

allowed to stand in the air a few minutes before being placed in the weighing bottle.

γ -Orcinolpthalein therefore combines with one molecule of hydrochloric acid gas. It is the only one of the three orcinolphthaleins that does this. It thus shows its great analogy to fluorescein which also combines with a molecule of hydrochloric acid gas.¹ When treated with fuming hydrochloric acid the γ -phthalein also forms the yellow hydrochloride.

Orcinoltetrachlorophthaleins.

The orcinoltetrachlorophthaleins were prepared by fusing tetrachlorophthalic acid with pure orcinol in the presence of zinc chloride, phosphorus pentoxide, concentrated sulfuric acid, or fuming sulfuric acid (containing 15% of free SO_3). The tetrachlorophthalic acid was the commercial product of Heller and Merz purified by the method of Delbridge.² The purity of the product used was checked by molecular weight determinations made by titrating a weighed sample with standard alkali.³

Subst., (I) 0.5781, (II) 0.3398; 0.1 N NaOH, (I) 37.03, (II) 21.72 cc. Calc. for $\text{C}_6\text{Cl}_4(\text{COOH})_2 \cdot 0.5\text{H}_2\text{O}$: mol. wt., 312.90; found: mol. wt., (I) 312.20, (II) 312.87.

Twenty grams tetrachlorophthalic acid, 19 g. orcinol, and 19 g. freshly fused zinc chloride were ground intimately, transferred to a 250 cc. round bottom flask and heated in a sulfuric acid bath to 160–170°. The reaction began at once, as indicated by the appearance of a red color, and the mixture soon formed a pasty mass which partly solidified at the end of two hours. The hard red mass was ground, dissolved in normal alkali by heating, the solution filtered, and acidified with hydrochloric acid. *Dark red flocks* separated. The mixture was then boiled with steam, and the crude orcinoltetrachlorophthaleins filtered off. The *dark red* product dried at 110° (28 g.) corresponded to a yield of 85%.

Phosphorus pentoxide was next used as the condensing agent. One hundred and fifty-six grams of tetrachlorophthalic acid, 145 g. of orcinol, and 140 g. of phosphorus pentoxide were ground together and fused as above. The contents of the flask melted to a red viscous mass which did not solidify in two hours. The mixture treated as before gave 162 g. of a *dark red* product, a yield of 65%.

The crude product obtained in these two syntheses could be separated into its isomers only with the greatest difficulty. Ether could not be satisfactorily used, as it had been in the case of the orcinolphthaleins (see p. 1216), owing to the fact that a dark red material caused the ether to form emulsions with the alkali, which were so stable that the process was slow and laborious. Sufficient amounts of the isomers were finally obtained, however, to show that this dark red material was an impurity and not a quinoid form of one of the isomers. Indeed it was found (see p. 1242) that this red material was formed by the decomposition of the β -orcinoltetrachlorophthalein itself in *hot* dilute alkaline solutions. Consequently, in the subsequent preparations the crude material was dissolved only in *cold* alkali.

Sulfuric acid was then used as the condensing agent. Fifty grams of tetrachlorophthalic acid, 48 g. of orcinol and 45 cc. concentrated sulfuric acid were heated to 135° for two hours. During the fusion the temperature rose to 150° for a short time. A

¹ THIS JOURNAL, 36, 701 (1914).

² *Am. Chem. J.*, 41, 414 (1909).

³ *Ibid.*, 41, 401 (1909).

secondary reaction set in as evidenced by the frothing of the mass, the formation of brownish tarry material, and the vigorous evolution of sulfur dioxide. This reaction almost entirely ceased, however, on lowering the temperature to 135° . At the end of two hours the melted mass was poured into water, the product filtered off and dissolved in *cold, dilute* alkali. On acidification the phthaleins separated as *light yellow* flocks. The mixture was heated to boiling with steam, the crude product filtered off and dried at 110° . Yield, 63%.

All of this product (46 g.) was separated into the isomers by the method given below and gave

| Isomer. | Grams. |
|----------------|--------|
| α | 11.0 |
| β | 17.0 |
| γ | 8.0 |

and in addition a large amount of tar.

Fuming sulfuric acid was next used as the condensing agent. Forty-one grams of tetrachlorophthalic acid and 20 cc. of fuming sulfuric acid were placed in a flask and heated to 150° for some time. The temperature was then lowered to 135° and 38 g. orcinol added. The reaction proceeded so slowly that 20 cc. more of fuming sulfuric acid were added. The reaction then proceeded, as indicated by the red color of the mixture. At the end of the two hours the product was treated exactly as in the preceding case. A *light yellow* product was obtained, which after drying at 110° weighed 57 g. corresponding to a yield of 88%. This material yielded the following amounts of the different isomers:

| Isomer. | Grams. |
|----------------|--------|
| α | 12.5 |
| β | 32.0 |
| γ | 7.5 |

On attempting to repeat this synthesis the temperature rose to 140° for a few moments. Instantly a vigorous secondary reaction began, accompanied by the evolution of sulfur dioxide. This reaction decreased somewhat when the temperature was lowered to 100° , but began again as soon as heat was applied. The product formed was largely tarry material, which contained only a small percentage of the phthaleins.

It seems from the results presented here that zinc chloride is the best condensing agent to use in the preparation of the orcinoltetrachlorophthaleins. The dark red decomposition products obtained from the material made with this condensing agent (see p. 1239) would probably not have been formed if it had not been dissolved in *hot* alkali.

The method used in isolating the isomeric orcinoltetrachlorophthaleins was very similar to that used in the case of the orcinolphthaleins (see p. 1217). γ -Orcinoltetrachlorophthalein is soluble in dilute solutions of the alkali carbonates and bicarbonates; β -orcinoltetrachlorophthalein is soluble in sodium carbonate solution, and is removed from its ethereal solution by aqueous solutions of this salt; α -orcinoltetrachlorophthalein is readily soluble only in solutions of potassium and sodium hydroxide and differs from α -orcinolphthalein in that it is not even *partially* removed from its ether solution by sodium carbonate solutions. The separation of the α - and β -isomers by ether and sodium carbonate is therefore complete.

The method used was as follows: The crude material was dissolved in cold normal alkali, and precipitated by pouring into dilute mineral acid. This mixture was then shaken with a large volume of ether, the aqueous layer drawn off, and the ether solution of the phthaleins filtered to remove tar. The ether solution was then shaken with one-fourth its volume of normal soda solution. This removed all the γ -compound, and a small amount of the β -isomer. The latter was extracted by shaking the soda solution with several portions of *fresh* ether. The crude γ -product obtained by acidifying this soda solution is only approximately pure, and is further purified as indicated below (see p. 1243). The ether solutions now contain the α - and β -compounds. The latter is removed by shaking with several portions of soda solution and then the former by means of sodium hydroxide solution.

α -Orcinoltrachlorophthalein.

The major part of the α -trachlorophthalein obtained as outlined above was dark colored, *i. e.*, contained tarry by-products, although some portions were perfectly white. The dark colored material after being recrystallized from ethyl acetate, methyl alcohol, and ethyl alcohol, was still straw colored. It was, however, nearly pure as shown by the following analysis made on material dried at 180°:

Subst., 0.3382; 0.1 N AgNO₃, 26.95 cc. Calc. for C₂₂H₁₂O₃Cl₄: Cl, 28.49; found: Cl, 28.26.

This material was purified by dissolving in ethyl alcohol and precipitating with water. The air dried substance lost 7.45% of its weight on heating to 180° and some moisture condensed on the cold part of the tube. The loss calculated for one molecule of alcohol would be 8.45%. It is quite likely therefore that this compound, like the α -orcinolphthalein crystallizes with one molecule of alcohol.

An attempt was made to obtain a colorless product by saponification of the pure diacetate (see p. 1242). Fifteen grams of the diacetate were suspended in 150 cc. of absolute alcohol, an equal volume of normal sodium hydroxide solution added, and the mixture boiled for 50 minutes. The solution was then filtered, diluted and acidified with sulfuric acid. Chocolate colored flocks separated, which when filtered off, and crystallized several times from different solvents were still colored pale yellow. The filtrate obtained after saponification gave no reaction for chlorides.

Pure α -orcinoltrachlorophthalein dissolves in alkalis with an almost *pure blue* color, having but a faint trace of red, thus differing markedly from α -orcinolphthalein. It is only slightly soluble in aqueous ammonia, and in sodium carbonate solutions. The fact that it is *not* removed from its ether solution by sodium carbonate solution while the α -orcinolphthalein is slowly extracted is unexpected, since this would seem to indicate that it unites with weak alkalis less readily than the mother substance. α -Or-

cinoltetrachlorophthalein is soluble in glacial acetic acid, methyl and ethyl alcohols, ethyl acetate and acetone. It is perceptibly less soluble in solvents than is the α -orcinolphthalein. When *absolutely pure* it is *colorless* and dissolves in alcoholic ammonia *without color*. The slightest trace of its isomers can thus be detected (see pp. 1243 and 1244). When water is added to this colorless solution it turns *blue* and after a few days' standing the *colorless* α -tetrachlorophthalein crystallizes out.

α -Orcinoltetrachlorophthalein Diacetate. — α -Orcinoltetrachlorophthalein was converted into the diacetate in the usual manner (see p. 1219). It was crystallized alternately from benzene and ethyl acetate until a perfectly white product was obtained which showed a constant melting point of 292° . A chlorine determination on a sample of this material dried at 180° gave the following result:

Subst., 0.3000; 0.1 *N* AgNO₃, 20.50 cc. Calc. for C₂₂H₁₀O₅Cl₄(CH₃CO)₂: Cl, 24.37; found: Cl, 24.23.

The diacetate is soluble in benzene, ethyl acetate, and acetone, and rather difficultly soluble in absolute alcohol. It crystallizes in minute, perfectly colorless rhombs. It is insoluble in water and in solutions of the alkalis, but is saponified readily on being heated in the latter. Some decomposition takes place even in the cold if alcoholic alkali be used (see p. 1241).

β -Orcinoltetrachlorophthalein.

The β -orcinoltetrachlorophthalein obtained by the method of separation described above contained a small amount of red material that imparted a faint pink tint to the product. Crystallization from methyl alcohol, ethyl alcohol, ethyl acetate and glacial acetic acid gave a product that was colorless, but on heating to 150° a faint pink tint appeared. It was shown to be pure by the following determinations made on material dried at 180° :

Subst., (I) 0.3153, (II) 0.2825, (III) 0.2830; 0.1 *N* AgNO₃, (I) 25.20, (II) 22.46, (III) 22.56 cc.

Calc. for C₂₂H₁₂O₄Cl₄: Cl, 28.49; found: Cl, (I) 28.34, (II) 28.19, (III) 28.27.

In order to determine whether this pink color was due to an impurity or to a quinoid form of β -tetrachlorophthalein, an attempt was made to obtain pure white material by the saponification of the pure β -orcinoltetrachlorophthalein diacetate (see p. 1243) with alcoholic caustic potash. The reaction began in the cold, as indicated by the production of a red color. The mixture was boiled on the water bath for one hour and filtered. A small amount of dark red, well crystallized material separated, presumably a potassium salt. The filtrate on dilution and acidification with sulfuric acid gave a precipitate of *dark red flocks, identical in properties with the dark red material* described above (see p. 1239). The filtrate from this product gave a strong reaction for chlorides. β -Orcinoltetrachlorophthalein there-

fore decomposes in hot alkaline solutions with the elimination of chlorine to give a substance which in the free state is dark red. The faint pink color noted in the β -orcinoltetrachlorophthalein is no doubt due to a trace of this material. The red crystalline material, presumably a potassium salt, was soluble in water, and this solution when acidified gave a red flocculent precipitate.

Pure β -orcinoltetrachlorophthalein is soluble in methyl and ethyl alcohols, acetone, glacial acetic acid, and ethyl acetate. It is soluble in alkalis with a smudgy red color intermediate between that of β -orcinolphthalein and tetrabromo- β -orcinolphthalein. From these solutions it is precipitated as a *white hydrate* by acids. A colored form of the free β -orcinoltetrachlorophthalein analogous to that obtained in the case of β -orcinolphthalein was never observed. In alcoholic ammonia it dissolves with a deep red color, but *without fluorescence*. It is thus possible to detect the presence of the slightest trace of the γ -compound (see p. 1244).

β -Orcinoltetrachlorophthalein Diacetate.— β -Orcinoltetrachlorophthalein was acetylated in the usual manner (see p. 1219). The brownish diacetate was crystallized from benzene, ethyl acetate, and ethyl alcohol until a perfectly white product was obtained, which showed the constant melting point of 239° . A chlorine determination was made on a sample dried for one-half hour at 180° .

Subst., 0.3330; 0.1 *N* AgNO₃, 22.73 cc.

Calc. for C₂₂H₁₀O₅Cl₄(CH₃CO)₂: Cl, 24.37; found: Cl, 24.20.

The diacetate is soluble in benzene, ethyl acetate, acetone, and rather difficultly soluble in absolute alcohol. It is insoluble in water, and in alkalis. Like the isomeric α -compound it undergoes decomposition when boiled with alcoholic potash (see p. 1242).

γ -Orcinoltetrachlorophthalein.

The crude γ -orcinoltetrachlorophthalein obtained from the ether solution of the mixture of the isomers (see p. 1241) by the first extraction with soda solution was quite impure, containing sufficient of the dark red material to prevent crystallization. It was converted into its diacetate, which was more readily purified, and the pure diacetate (see p. 1244) saponified with half normal alcoholic potassium hydroxide. The solution was filtered, diluted and acidified. Perfectly white flocks separated which crystallized from methyl alcohol by the addition of water in fine, white needle clusters. After drying in the air, a sample heated to 180° for one-half hour came to constant weight without change of color and moisture condensed on the cool part of the tube.

Subst., (I) 0.4672, (II) 0.2484; loss, (I) 0.0310, (II) 0.0165.

Calc. for C₂₂H₁₀O₅Cl₄·2H₂O: H₂O, 6.88.

Calc. for C₂₂H₁₀O₅Cl₄·CH₃OH: CH₃OH, 6.04; found: (I) 6.63, (II) 6.64.

A chlorine determination on the anhydrous material gave the following result:

Subst., 0.3234; 0.1 *N* AgNO₃, 25.93 cc. Calc. for C₂₂H₁₂O₅Cl₄: Cl, 28.49; found: Cl, 28.43.

γ -Orcinoltetrachlorophthalein possesses practically the same solubilities in the ordinary organic solvents as the α - and β -isomers. It is, however, more readily soluble in aqueous ammonia and in alkali bicarbonates than its isomers. Its dilute alkaline solutions are yellow and show a green fluorescence which is apparently greater than that of γ -orcinolphthalein. Evidence on this point was obtained by dissolving molecular equivalent quantities of the two compounds in equal amounts of tenth normal alkali and comparing the two. When dissolved in alcoholic ammonia the solution has a reddish yellow color and a marked *greenish* fluorescence.

γ -Orcinoltetrachlorophthalein Diacetate.—The crude reddish brown phthalein was acetylated in the usual manner (see p. 1219). The brownish diacetate was crystallized alternately from benzene and ethyl acetate till a perfectly white compound was obtained which showed the constant melting point of 252–253°. This material dried for one-half hour at 180° was analyzed.

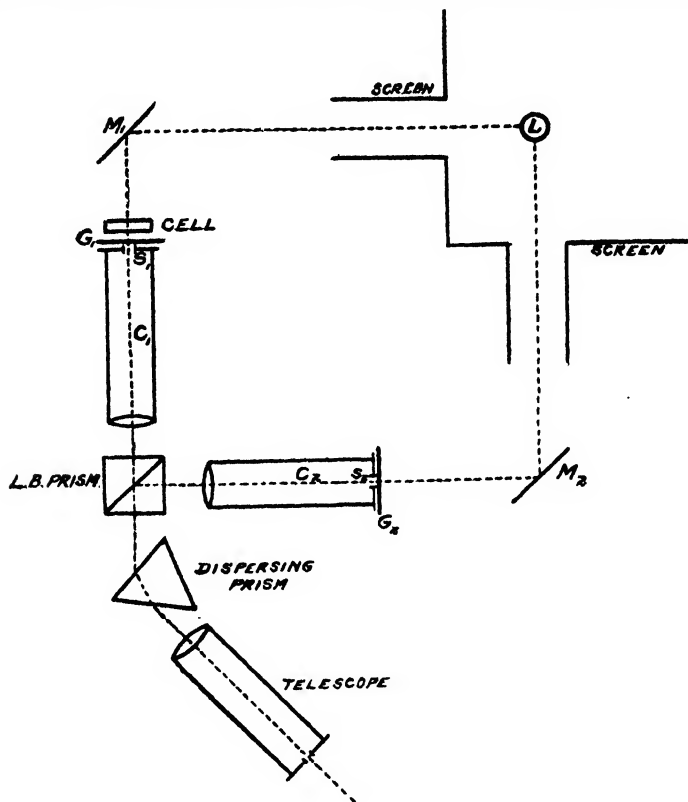
Subst., 0.2778; 0.1 *N* AgNO₃, 19.03 cc. Calc. for C₂₂H₁₀O₅Cl₄(CH₃CO)₂: Cl, 24.37; found: Cl, 24.29.

The diacetate is soluble in benzene, ethyl acetate, and acetone; rather difficultly soluble in absolute alcohol. From benzene it crystallizes in long, flat needles. It is insoluble in water and in alkalis, but is saponified by the latter on heating or slowly in the cold in the presence of alcohol.

Absorption Spectra of the Orcinolphthaleins, the Tetrabromoorcinolphthaleins, and the Orcinoltetrachlorophthaleins.

For absorption spectra studies weighed amounts of the pure phthaleins were dissolved in potassium hydroxide solutions of such strength that four molecules of alkali were present to each molecule of phthalein. In the case of the β - and γ -derivatives alcoholic potassium hydroxide was used, but in the case of the α -compounds aqueous alkali was used because of the tendency of these phthaleins to assume the carbinol form in the presence of alcohol. The absorption bands were studied by means of transmission curves. This work was carried out by Professor Gibbs and Mr. K. S. Gibson of the Physics Department. The following description and figures, taken from their report explain the methods used and the results obtained: "The observations were made by means of a Lummer-Brodhun spectrophotometer (see p. 1245). Light from the acetylene flame *L*, was reflected into the collimators *C*₁ and *C*₂ by mirrors, *M*₁ and *M*₂. Ground glass plates, *G*₁ and *G*₂, were placed in front of the slits in order to produce a uniform field. After passing through the collimators light passes through the Lummer-Brodhun prism, and is then dispersed and

observed by the telescope. The liquid to be observed is placed in the cell opposite the slit S_1 . The slit in the telescope and the slit S_1 were set at equal widths and kept constant, while the observations were made by varying the width of slit S_2 until the two fields were of equal intensities.



LUMMER-BRODHUN SPECTROPHOTOMETER.

Fig. 1.

On account of the large variation in the absorption of liquids, cells of various widths were used, and in some cases it was necessary to use capillary films, which was done by putting a small amount of liquid in a cell and drawing the liquid up on one side by means of a piece of glass placed at one edge. In this way, a wedge-shape film of various widths was secured. In all cases, a cover was kept on the cells in order to prevent evaporation of the alcohol, and in all cases observations made towards the end of the run checked with those made at the beginning, indicating that very little evaporation had occurred. This precaution was found very necessary either because of the evaporation of the alcohol or because

of the absorption by the liquid of something from the atmosphere, possibly carbon dioxide. In the accompanying curves the percentage of transmission is computed by dividing the observation made with the cell removed, by the observation made with the cell and liquid in place, due correction having been made for reflection at the boundary of the glass and air and at the boundary of the glass and liquid, which, in the case of the capillary film, required a correction for four boundaries of glass and air and two of glass and liquid. The wave lengths of the points of minimum transmission, *i. e.*, of maximum absorption are shown in the following table:"

| | Wave lengths. | | |
|---|---------------|-----------|------------|
| | α . | β . | γ . |
| Orcinolpthaleins..... | 0.528 | 0.536 | 0.498 |
| Orcinoltetrachlorophthaleins..... | 0.562 | 0.554 | 0.521 |
| Tetrabromoorcinoiphthaleins..... | 0.572 | 0.576 | 0.529 |
| Tetrabromoorcinoiltetrachlorophthalein (very dilute solution) | | | 0.555 |

In the study of these absorption curves it will be noticed that in every case the absorption bands are gradually shifted towards the red end of the spectrum as we pass from the orcinolphthaleins to their bromine and chlo-

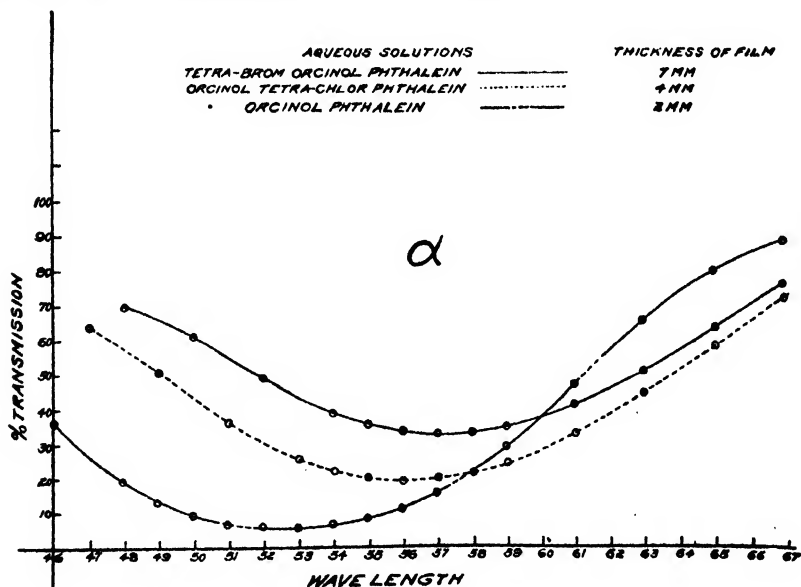


Fig. 2.

rine derivatives, just as was found to be the case in the study of the absorption spectra of fluorescein, eosin, tetrachlorofluorescein and tetrachloroeosin.¹

¹ THIS JOURNAL, 36, 680 (1914).

Again, the shifting caused by the entrance of *four* chlorine atoms into the *phthalic acid* residue of γ -orcinolphthalein is almost the same as that

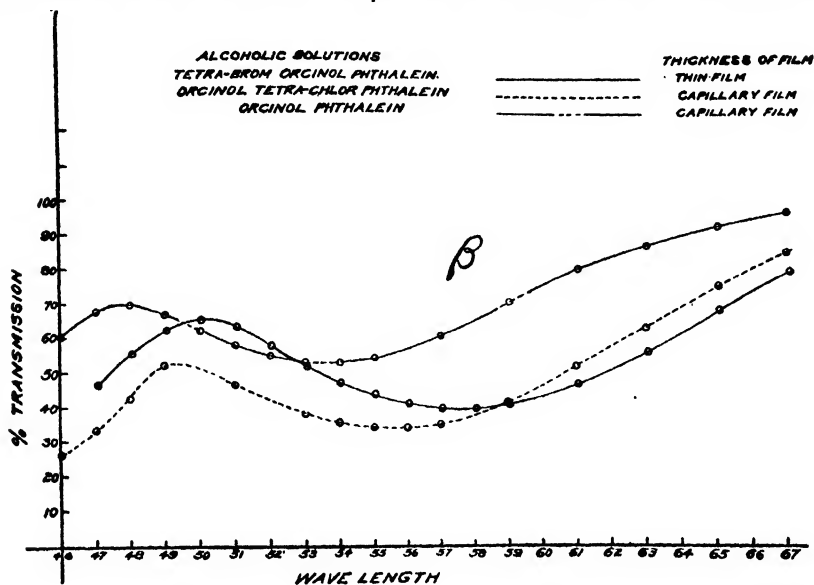


Fig. 3.

caused by introducing *two* bromine atoms into *each* of the two residues of orcinol, *i. e.*, the shifting is proportional to the *number* of halogens

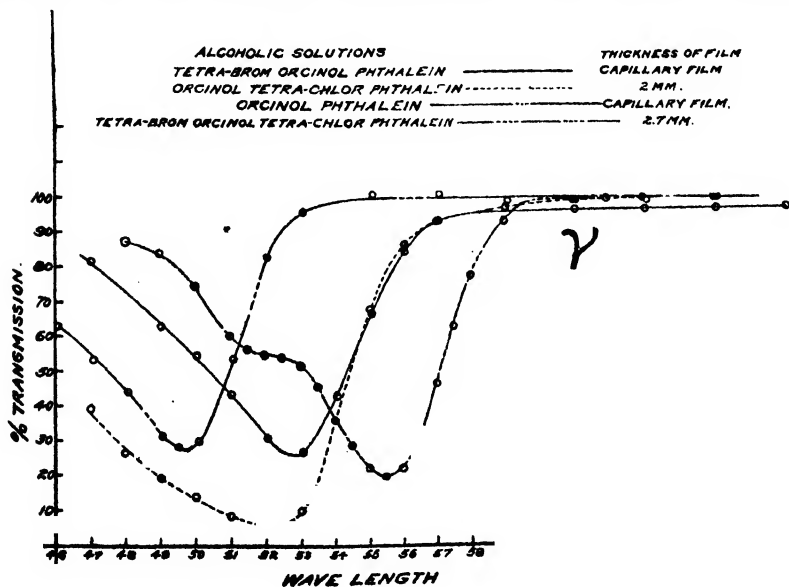


Fig. 4.

introduced, rather than to the increase in molecular weight. For example, the absorption bands of γ -orcinoltetrachlorophthalein and of tetrabromo- γ -orcinolphthalein are very nearly identical, while the molecular weights of these substances are 498 and 676.

It is interesting to note that only one absorption band is to be seen here in the case of the γ -orcinolphthalein and its halogen derivatives, while *two* were observed in the case of fluorescein and its chlorine and bromine substitution products. For this reason it seemed of importance to make the tetrabromo- γ -orcinoltetrachlorophthalein and examine its spectrum. This substance was prepared and analyzed by Mr. J. J. Kennedy. An examination of its absorption curve (see p. 1247) shows one band at 0.555 and there is evidence of another at approximately 0.520. The shape of the curves of β -orcinolphthalein and its chlorine and bromine derivatives (see p. 1247) also shows evidence of *two bands*, the second one, however, in this case being on the boundary between the visible and the ultraviolet part of the spectra.

The curves for the γ -phthaleins are the typical curves found for fluorescent substances, and these phthaleins are unquestionably derivatives of fluorescein, and have, therefore a similar chemical structure.

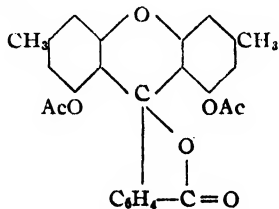
Theoretical.

As pointed out above R. Meyer (see p. 1203) suggested Formula III for γ -orcinolphthalein, and Baeyer (see p. 1208) concluded that α -orcinolphthalein possesses the vicinal or symmetrical structure represented by Formula I. This leaves the unsymmetrical Formula II (see p. 1203) as the only one possible for the β -compound.

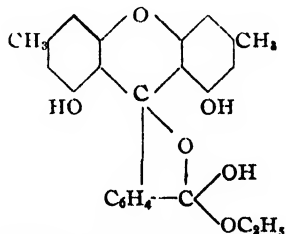
While there seems to be but little doubt regarding the correctness of Formula III assigned to γ -orcinolphthalein by R. Meyer, because of the marked analogy of this compound and its tetrabromo derivative to fluorescein and eosin, the evidence furnished by Baeyer (see pp. 1208 and 1210) in regard to the structure of α -orcinolphthalein is perhaps less conclusive. However, Formulas I for the α -compound and II for the β -isomer are in accord with all the known facts. According to this arrangement β -orcinolphthalein would be expected to possess properties intermediate between those of the α - and γ -isomers. In general this is the case. For example, the γ - is the strongest acid and the α -compound the weakest, while the β - is intermediate between these two. The free γ -compound exists only in the quinoid form, the β - in the lactoid and quinoid forms while the α -compound is known only in the lactoid modification. The γ -compound is the one most disposed to the formation of colored salts with acids. It evidently forms a salt even with acetic acid, as the pure material precipitated from alkaline solution by this acid is at first *colored* but on standing becomes *colorless*, just as does the compound of the β -isomer when precipitated with a *mineral acid*. In both cases this color change is

probably due to hydrolysis of the colored salts of the acids. This is in accord with the fact that dry hydrochloric acid gas unites with the γ -compound while it is without action on the α - and the β -phthaleins. As pointed out by Kehrmann the β -compound is, in turn, clearly more disposed to the formation of salts with acids than is the α -compound. The nature of the absorption spectra also is in agreement with the supposition that the β -phthalein occupies a position intermediate between that of the α - and γ -isomers. It is also interesting to note that the melting point of the γ -diacetate is 207° ; that of the β -compound 227° , and of the corresponding α -isomer 247° . However, as this relation does not hold in the case of the diacetates of the orcinoltetrachlorophthaleins, it perhaps should not be considered as having too much weight.

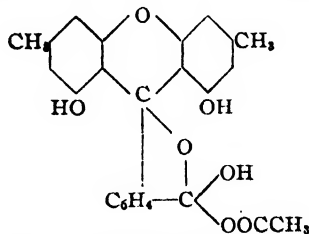
α -Orcinolphthalein, its diacetate and dibenzoate, its compound with ethyl alcohol and with acetic acid, are all colorless and hence have lactoid formulas:



α -Orcinolphthalein diacetate and dibenzoate.



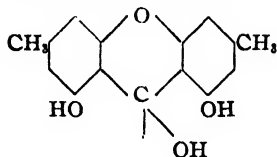
Compound of α -orcinolphthalein with ethyl alcohol.



Compound of α -orcinolphthalein with acetic acid.

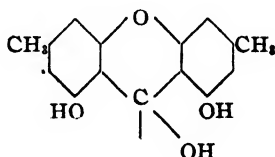
The colorless monopotassium salt formed from α -orcinolphthalein is represented as a derivative of the carbinolcarboxylic acid, Formula I (see p. 1250). As it is formed in alcoholic solution, and, when freshly prepared, loses approximately three molecules of alcohol and one of water when heated and *becomes colored*, it is represented by Formula II. On standing in the air all the alcohol is given off but not the water of constitution. Formula II without the alcohol represents this compound. Both these forms of the monopotassium salt must be considered as derivatives of the α -carbinolcarboxylic acid (I), since they are *colorless* and on heating lose water and alcohol or water alone and go over to the *colored ortho-quinoid form* (III) (see below). The lactoid formula (see p.

1209) proposed by Baeyer for this colorless monopotassium salt is not in accord with this behavior.



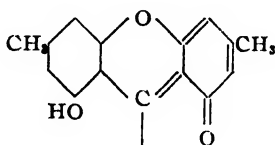
α -Orcinolphthalein carbinolcarboxylic acid, colorless.

(I).



Monopotassium salt carbinol form, colorless.

(II).



Monopotassium salt, *o*-quinoid form, colored.

(III).

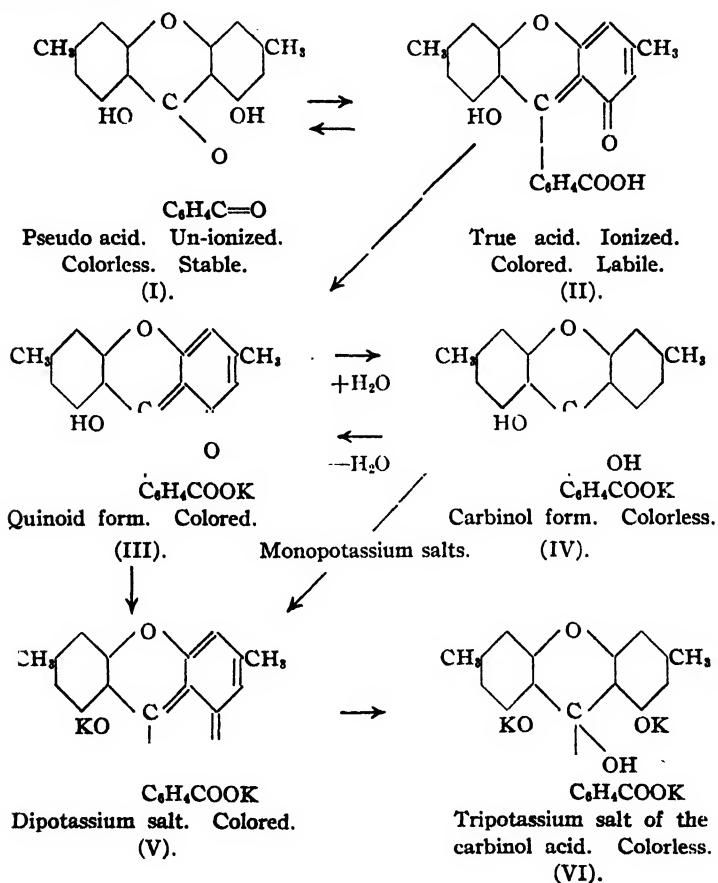
The steps involved in the changes of color which α -orcinolphthalein undergoes when treated with alkalis as proposed by Baeyer are given on p. 1209.

In the light of the results obtained in this investigation, this explanation is certainly untenable because analyses show: (1) that the first violet salt is the *quinoid form* of the *monopotassium salt*, and not the *dipotassium salt*; and, (2) that the *colorless monopotassium salt* is the *carbinol form* of the first violet salt, and (3) that the *violet* and *blue* salts are *mono-* and *dipotassium* salts, respectively, and not *di-* and *tetrapotassium* salts as stated by Baeyer.

The explanation of the color changes that is in accord with all the facts is the following: α -Orcinolphthalein is a very weak acid but forms moderately stable sodium or potassium salts. It therefore belongs to the class of pseudo acids. Such substances Hantzsch¹ considers as existing in tautomeric forms, the one practically un-ionized acid, the other considerably ionized and which gives rise to the stable salts. Applying this to α -orcinolphthalein, we have the following explanation of the color changes: The violet color first observed is due to the formation of the *quinoid form* of the *monopotassium salt* (III, p. 1251) by the neutralization of the true acid (II) formed from the pseudo acid (I). In alcoholic solution this color disappears because alcohol favors the conversion of the colored *monopotassium salt* (III) into the colorless salt of the carbinol

¹ Ber., 32, 575 (1899); 35, 210, 226, 1001 (1902); 39, 139, 1073 (1906).

acid (IV), which is practically insoluble in alcohol. On the addition of more alkali both these salts are converted into the blue dipotassium salt (V) which, in the presence of a large excess of alkali, is converted into the colorless tripotassium salt of the carbinol acid (VI). On boiling with water all these salts undergo hydrolysis to alkali and the true acid (II) which then crystallizes in the form of the pseudo acid (I) which is insoluble in water.



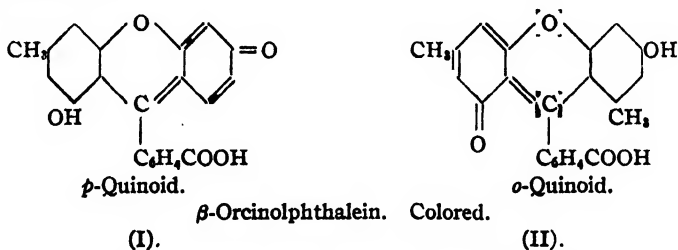
One difference between this explanation and that of Baeyer is that in this case the potassium is represented as replacing hydrogen of the carboxyl group. Since in the true acid (II) a weak acid group (OH) and a strong acid group (COOH) exist, the stronger group would be neutralized first, *i. e.*, the first atom of potassium would replace the hydrogen of the carboxyl group. This is in agreement with the fact that the monopotassium salt is *colored* or may be readily converted into the colored form by heating. According to Baeyer, however, the potassium replaces the

hydrogen of the phenol group, and the colorless salt has the lactoid structure. This structure does not agree with the fact that the colorless salt readily becomes colored on heating. This change is, however, very readily accounted for by the carbinol form assigned to the colorless monopotassium salt in the explanation given above.

Another difference between this explanation and that of Baeyer is that the pyrone ring is here represented as remaining intact. This is proved by the fact that even with a large excess of potassium hydroxide a *tripotassium* salt of the carbinol carboxylic acid (VI, p. 1251) is formed and not a *tetrapotassium* salt as represented by Baeyer (see p. 1209). A further proof that the pyrone ring is not ruptured is the fact that α -orcinolphthalein when benzoylated by the Baumann-Schotten reaction in strong alkaline solution gives a *dibenzoate* and not a *tetrabenzoate* (see pp. 1203 and 1219).

It is interesting to note that α -orcinolphthalein (see Formula I, p. 1251), in which both hydroxyl groups are *ortho* to the methane carbon atom, reacts with alkalis to form *colored* and *colorless* salts in exactly the same manner as those phthaleins in which the hydroxyl groups occupy the *para* positions to the methane carbon atom.

β -Orcinolphthalein exists in a colored modification represented by Formulas I or II.



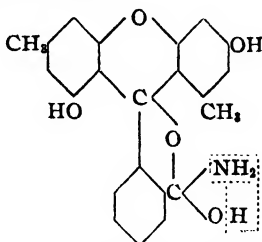
and in a colorless modification represented by Formula II on p. 1203.

The lactoid modification is obtained by heating the hydrate, or the compound of β -orcinolphthalein with acetic acid, to 150° , the quinoid modification by heating the lactoid form to 180° , and by crystallizing the phthalein from *hot* alcohol or *hot* glacial acetic acid. As pointed out above (see p. 1228) it is the stable, and the lactoid the unstable form.

From the close resemblance in color of the quinoid form of the β -phthalein to that of the γ -phthalein, which is only known in the quinoid modification, and the fact that the α -phthalein is only known in the lactoid form, it seems highly probable that the *paraquinoid* formula is the one which best represents the structure of the *colored* modification of β -orcinolphthalein.

The difference in the action of dry ammonia gas on the two forms of the β -phthalein is rather surprising. From the resemblance of the quinoid form to the γ -phthalein it might have been expected that this modification

of the β -phthalein would have absorbed ammonia just as the γ -isomer does, while the lactoid form bearing such a close resemblance to the α -phthalein, which is only known in the lactoid form, and which does not absorb ammonia at all, might naturally have been expected to be unacted on by this gas. Just why the lactoid form absorbs ammonia and the quinoid does not it is not possible to say, but it seems to be connected with the fact that the lactoid form gives a colorless hydrate. As the compound with ammonia has no color it may have a structure like that assigned to the hydrate (see below).

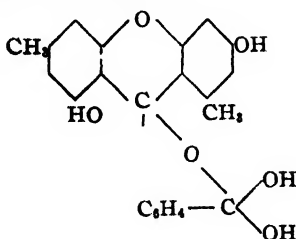


Compound of β -orcinolphthalein with ammonia.
Colorless.

This substance loses a molecule of ammonia when heated and gives the lactoid form of the phthalein, just as the hydrate does when it loses a molecule of water. Its close connection with the hydrate is also shown by the fact that it loses all its ammonia in the air and takes up moisture in its stead to form the hydrate (see p. 1229).

The statement of Fischer that orcinolphthalein forms a monacetate, and of Meyer, that the β -orcinolphthalein contains one-third of a molecule of water (see p. 1206) are both incorrect. Meyer's β -orcinolphthalein was evidently an impure product.

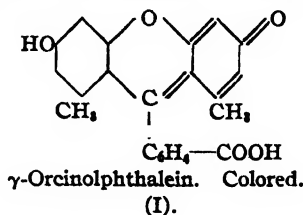
β -Orcinolphthalein hydrate is colorless and gives the colorless lactoid modification of the phthalein when heated to 150° . It is hence represented as derived from the lactoid modification:



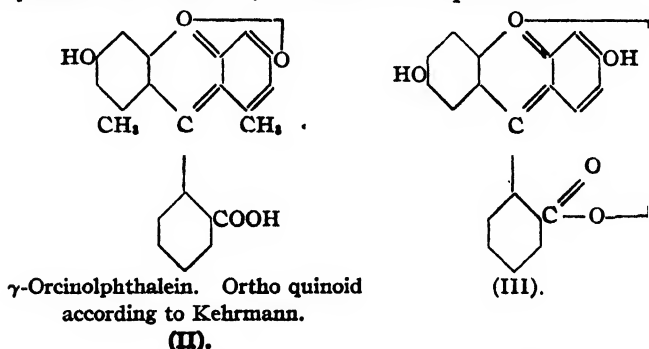
β -Orcinolphthalein hydrate.

The diacetate, dibenzoate and the compound of β -phthalein with acetic acid are also colorless and are represented by lactoid formulas analogous to those given for the corresponding α -compounds (see p. 1249).

γ -Orcinolpthalein in the free condition is only known in the *colored* modification represented by the quinoid Formula I.



The *ortho* quinoid formula (II) assigned to this phthalein by Kehrman is probably incorrect. If, as Kehrman assumes, the pyrone oxygen becomes tetravalent, *i. e.*, assumes basic properties it would unite with the stronger acid group, *i. e.*, with the carboxyl. If, then, the *ortho* quinoid formula be assumed, Formula III is preferable to II.

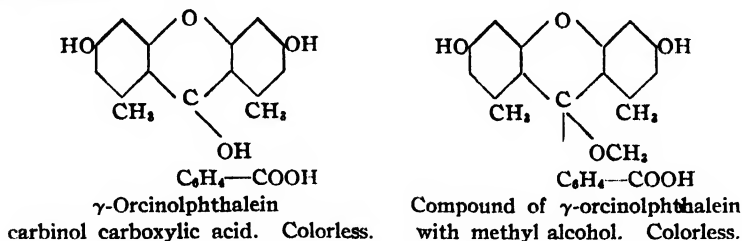


From the great resemblance of γ -orcinolpthalein to fluorescein (see pp. 1234, 1237, 1238 and 1239) it seems much more probable that both substances have the *para*-quinoid structure. From the structural formula (I) for γ -orcinolpthalein given above it will be seen that it is represented as a dimethyl fluorescein. Like fluorescein, γ -orcinolpthalein has both *acid* and *basic* properties. It unites with dry ammonia gas to form a *colored diammonium salt* (see p. 1238), and it is the only one of the orcinolpthaleins which acts in this way. It is also the only one of the orcinolpthaleins to combine with *dry hydrochloric acid gas* to form a *colored hydrochloride*. It is thus *at the same time the most acid and the most basic* of the orcinolpthaleins.

γ -Orcinolpthalein hydrate, the compound with methyl alcohol, the diacetate, and the dibenzoate are all colorless and hence are all derivatives of the lactoid tautomeric modification (see Formula III on p. 1203) and must therefore be assigned lactoid formulas analogous to those given for the corresponding α - and β -compounds (see pp. 1249 and 1253).

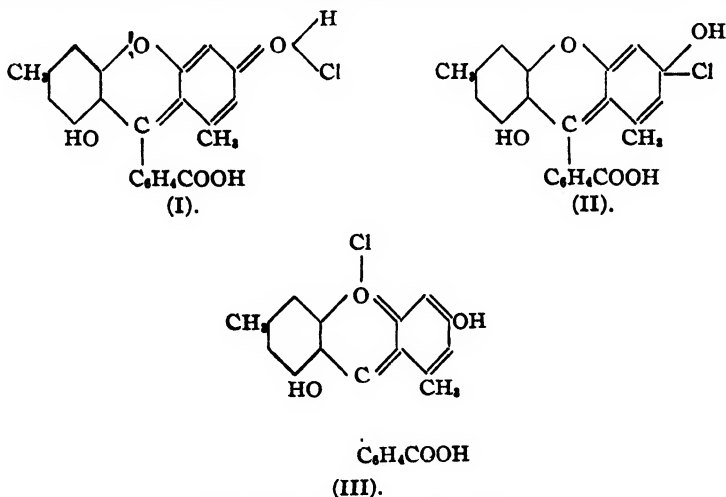
As the γ -orcinolpthalein hydrate loses water and the compound with methyl alcohol loses alcohol when heated and form the *yellow anhydrous*

phthalein, they might be regarded as carbinol forms of this phthalein as shown below:



The ease with which the hydrate loses water (see p. 1236), however, would seem to favor the assumption that the two hydroxyl groups from which the water is formed are combined with the same carbon atom as shown in the formula given for the hydrate (see p. 1253).

The hydrochlorides of the orcinolphthaleins are all colored and are therefore derivatives of the quinoid forms of these substances. They may be assigned the ordinary oxonium Formula I, the carbonium Formula II, or the ortho quinoid oxonium Formula III, analogous to those proposed by Kehrmann for the oxonium salts of the methylated orcinolphthaleins.¹



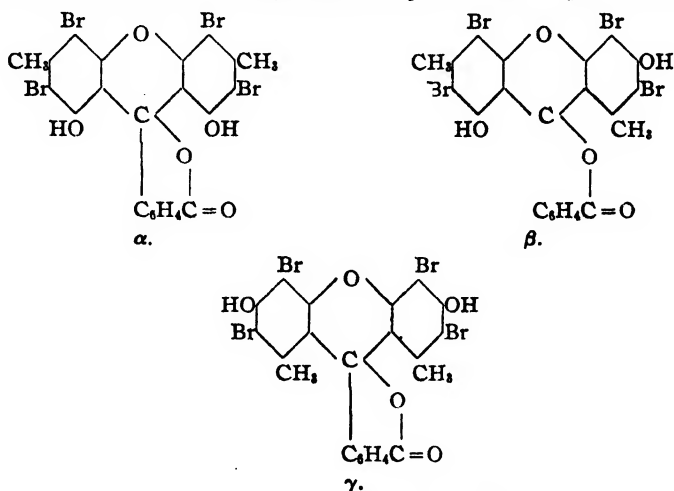
β -Orcinolphthalein hydrochloride.

We may also assign the *o*-quinoid structure instead of the above *p*-quinoid (Formulas I and II) to this hydrochloride.

The hydrochlorides of the isomeric α - and γ -phthaleins may be represented by formulas analogous to the above, bearing in mind that in the case of the γ -compound only the *p*-quinoid structure can be assigned to the ordinary oxonium salt and carbonium salt, while in the case of the α -orcinolphthalein only the *o*-quinoid structure is possible.

¹ *Ber.*, 45, 3506 (1912).

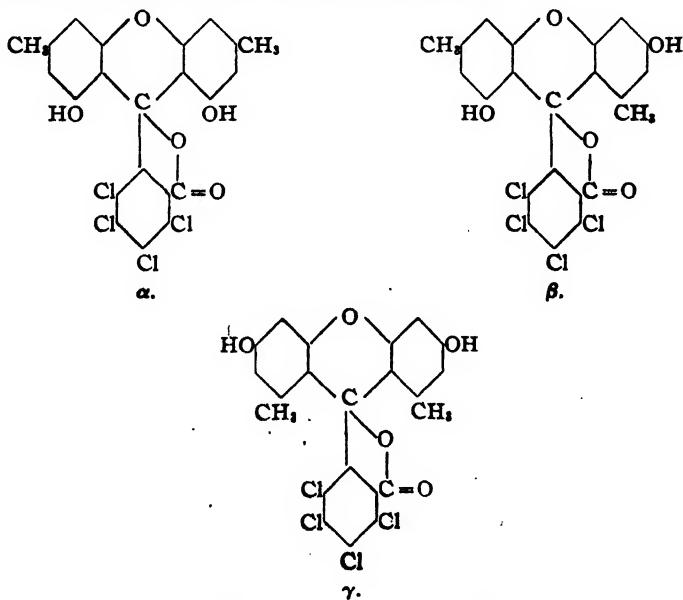
In the tetrabromoorcinoiphthaleins, the bromine is undoubtedly in the two orcinol residues exactly as in the case of eosin. As these compounds are all colorless they are best represented by the following lactoid formulas:



Tetrabromoorcinoiphthaleins.

The colorless tetrabromoorcinoiphthalein diacetates undoubtedly possess structures exactly analogous to those of the orcinolphthalein diacetates.

The orcinoltetrachlorophthaleins which are all colorless possess the structures represented by the following formulas:

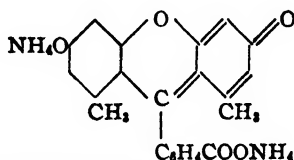


Orcinoltetrachlorophthaleins.

The formulas for the orcinoltetrachlorophthalein diacetates are derived by simple replacement of the phenol hydrogens of the above formulas by acetyl groups in each case.

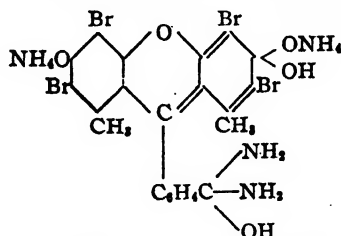
It is interesting to note that in each case in which chlorine or bromine atoms have been introduced into the phthalein molecule, the tendency to assume the free quinoid form is reduced. This is in accord with the following observation of Orndorff and Hitch. "Fluorescein in the free state exists only in the *colored* quinoid form. No colorless free fluorescein has ever been prepared. Tetrachlorofluorescein, on the other hand, has been obtained in two modifications, *colored* and *colorless*, but the colored form is the more stable. Eosin in the free state is flesh colored, and may be a mixture of the two forms, while the free tetrachloroeosin is colorless or very slightly colored. The colored modification has not yet been prepared.¹"

In the case of γ -orcinolphthalein dry ammonia acts on this compound with the formation of a colored diammonium salt which probably has the following formula:



Diammonium salt of γ -orcinolphthalein.

In the case of the tetrabromo- β -orcinolphthalein and tetrabromo- γ -orcinolphthalein four molecules of ammonia are absorbed, which is probably best represented by such a formula as the following:



Compound of tetrabromo- γ -orcinolphthalein
with four molecules of ammonia.

The successive steps of polyammonium salt formation have been worked out by Orndorff and Hitch² in connection with tetrachlorofluorescein and tetrachloroeosin.

Summary.

The results obtained in this investigation may be briefly summarized as follows:

¹ THIS JOURNAL, 36, 680 (1914).

² *Ibid.*, pp. 717 and 722.

1. The methods of preparing the orcinolphthaleins and of separating the isomers have been improved. The effect of conditions of preparation on the amounts of the isomers formed has also been studied.
2. The action of ammonia on γ -orcinolphthalein, on tetrabromo- β -orcinolphthalein, and on tetrabromo- γ -orcinolphthalein has been investigated.
3. The *colorless* and *colored* potassium salts of α -orcinolphthalein have been again prepared and analyzed and an explanation of the color changes of α -orcinolphthalein with alkalis more in accord with the facts than that proposed by Baeyer, has been suggested.
4. α -Orcinolphthalein exists only in the colorless form, while both colored and colorless forms of the isomeric β -compound have been prepared. The γ -phthalein is only known in the colored form. The tetrabromo-orcinolphthaleins and the orcinoltetrachlorophthaleins exist only in the colorless forms.
5. The colored compounds of the orcinolphthaleins with hydrochloric acid have been isolated and analyzed.
6. Colorless hydrates, acetyl and benzoyl derivatives, and colorless compounds of the orcinolphthaleins with solvents have also been prepared.
7. The three tetrabromo-orcinolphthaleins and the three orcinoltetrachlorophthaleins and their diacetates have been made and studied.
8. The absorption spectra of the orcinolphthaleins, of the tetrabromo-orcinolphthaleins, of the orcinoltetrachlorophthaleins and of the tetrabromo- γ -orcinoltetrachlorophthaleins have been investigated and the transmission curves plotted.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]
***o*- AND *p*-CHLOROBENZOYLACETIC ESTERS AND SOME OF
THEIR DERIVATIVES.**

By LAMBERT THORP AND E. R. BRUNSKILL.

Received March 16, 1915.

The work presented in this article is a continuation of that begun by one of us upon the halogenated benzoylacetic esters,¹ and had for its object a study of the effect of negative substituents in the aromatic nucleus upon the ease of alkylation and upon the course of the saponification of the substituted benzoylacetic esters. In regard to ease of alkylation the chlorobenzoylacetic esters stand between benzoylacetic ester and its nitro derivatives, a condition of affairs which might be expected *a priori* from other well-known instances of the effect of a substitution of a nitro group for a chlorine atom, such as the relative instability of chloroacetic and nitroacetic acids with respect to the loss of carbon dioxide, the difference

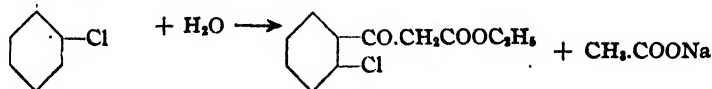
¹ THIS JOURNAL, 35, 270 (1913).

in the orientating influence of the halogen atom and the nitro group upon the entrance of a second substituent into the benzene ring, the more pronounced effect of the nitro group upon the reactivity of a halogen atom in the aromatic nucleus, etc.

The ketonic decomposition of *o*-chlorobenzoylacetate ester, by means of dilute sulfuric acid, is effected with the same degree of smoothness as obtains in the case of benzoylacetate ester itself, although with even dilute alkali the acid decomposition appears to predominate in the case of certain derivatives of *p*-chlorobenzoylacetate ester.

Experimental.

***o*-Chlorobenzoylacetate Ethyl Ester.**—To one-half (160 cc.) of a solution of sodium ethylate, prepared by dissolving 20.7 g. of sodium (2 equiv. wts.) in 320 cc. of absolute alcohol, 58.5 g. (1 mol) of acetoacetic ester were added. The solution of sodium acetoacetic ester, so obtained, was cooled to 5°, and then 28.25 cc. (0.5 mol) of *o*-chlorobenzoyl chloride were gradually admitted from a buret, the temperature of the reaction mixture being maintained under 12°. It is important that the solution be constantly stirred during this addition. After the lapse of half an hour 80 cc. of the sodium ethylate solution were added and, when the temperature of the mixture had become sufficiently low, 14.12 cc. of the acid chloride were dropped in as before. In this way, always employing one-half of the remaining sodium ethylate and *o*-chlorobenzoyl chloride, the operation was completed after five successive additions. In order that the separation of the sodium salt might be complete, the reaction mixture was allowed to remain in a cold place for 24 hrs. The salt was filtered with the aid of suction, and washed several times with dry ether. Yield, 123 g. Whereas the sodium salts of other tautomeric esters of this series are distinctly yellow in color, the sodium salt of *o*-chlorobenzoylacetate ester is pure white. When warmed with dilute ammonia solution it is decomposed in accordance with the scheme:



One hundred and twenty grams of the sodium salt of *o*-chlorobenzoylacetate ester were dissolved in 600 cc. of water, 54 g. of ammonium chloride and 60 cc. of concentrated aqueous ammonia were added, and the solution maintained at a temperature of 40–50° for 2–3 hrs., with frequent shaking. The product, which had separated as a heavy, yellow oil, was extracted with ether. The ethereal solution was dried over calcium

chloride, the ether removed, and the residue placed over sulfuric acid *in vacuo*. The yield of ester amounted to 70 g.

o-Chlorobenzoylacetate is a pale yellow, viscous liquid, heavier than water, and possessing a faint, though pleasant, aromatic odor. It is only very slightly soluble in water, but miscible with the common organic solvents. It cannot be distilled under 30 mm. pressure without suffering decomposition.

0.4364 g. subs. required 20.4 cc. 0.1 *N* AgNO₃. Calc. for C₁₁H₁₁O₂Cl: Cl, 15.6; found: 15.1.

Ketonic Decomposition of *o*-Chlorobenzoylacetate Ester. *o*-Chloroacetophenone.—In a flask, provided with a reflux condenser, a mixture of 54 g. of the ester, 240 cc. of water and 60 cc. of concentrated sulfuric acid was boiled until the evolution of carbon dioxide had apparently ceased, a condition which seemed to have been realized after 10–12 hrs. The mixture was cooled, and the ketone, which floated as an oily layer on the surface of the acid, was taken up with ether. In order to remove any unchanged ester the ethereal solution was shaken with 10% potassium hydroxide solution; it was then washed with water, separated and dried over calcium chloride. After the ether had been removed the residual ketone distilled entirely between 223 and 230°. After further fractionation, a pure product, boiling at 227–228° under 738 mm., was obtained in a yield of 80% of the theoretical.

o-Chloroacetophenone is a colorless liquid, very slightly soluble in water, and with a very agreeable, aromatic odor. The index of refraction was determined by means of an Abbé refractometer.

$n_{D_{25}^{\circ}} = 1.685$. Specific gravity: $d_{25}^{25} = 1.1884$.

0.2000 g. subs. required 12.92 cc. 0.1 *N* AgNO₃. Calc. for C₈H₇OCl: Cl, 22.94; found: 22.88.

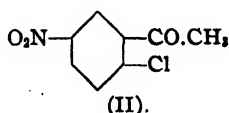
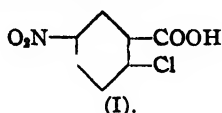
***o*-Chloroacetophenone Oxime.**—To a solution of 3 g. of hydroxylamine hydrochloride and 2 g. of sodium hydroxide in 10 cc. of water, 5 g. of the ketone were added, and then sufficient alcohol, 20 cc., to make the mixture homogeneous. The oxime began to crystallize from the solution after the latter had remained at room temperature for 3 hrs., and after 24 hrs. the separation appeared to be complete. The product was filtered, and hot water added to the filtrate, whereupon a further quantity of oxime was obtained. Recrystallization from 50% alcohol furnished a pure product in a yield of 90% of the theoretical.

o-Chloroacetophenone oxime crystallizes in the form of beautiful, silky needles which melt at 103°. The substance is very slightly soluble in cold water, more readily in hot water; slightly soluble in ligroin; easily soluble in alcohol or benzene; very easily soluble in ether or chloroform.

0.2448 g. subs. gave 19.0 cc. N₂ (24°, 743 mm., over KOH). Calc. for C₈H₇ONCl: N, 8.27; found: 8.56.

Nitration of *o*-Chloroacetophenone.—One hundred grams of nitric acid (sp. gr. 1.52) were cooled to 0°, and then 10 g. of *o*-chloroacetophenone were added gradually by means of a dropping funnel, the mixture being constantly stirred and the temperature maintained below 5°. After the solution had been allowed to remain in the freezing mixture for 3 hrs. it was poured into 500 g. of ice water, whereupon the nitro compound separated as a white, flocculent precipitate. The product was filtered, washed thoroughly with water and then recrystallized from alcohol. Yield, 85% of the theoretical.

The orientation of the nitro group in the nitrochloroacetophenone was effected by oxidation with a 2% potassium permanganate solution. The nitrochlorobenzoic acid obtained by this oxidation process showed a melting point of 164.7°. To the acid whose structure is represented by Formula I the literature assigns a melting point of 165°; consequently the ketone must have the nuclear substituents in the positions as represented by Formula II:



2-Chloro-5-nitroacetophenone crystallizes from alcohol in the form of small, colorless prisms, and has a melting point of 62°. It is insoluble in water, very slightly soluble in ligroin, slightly soluble in cold alcohol or ether, readily soluble in benzene, chloroform or hot alcohol.

0.2423 g. subs. gave 0.1752 g. AgCl. Calc. for $C_8H_6O_3NCl:Cl$, 17.77; found: 17.88.

***p*-Chlorobenzoyl-acetic Ester.**—This ester was obtained in a manner analogous to that for the preparation of the corresponding ortho compound, as outlined above. It was found advantageous, however, to employ the *p*-chlorobenzoyl chloride in ether solution since, under these circumstances, the separation of the sodium salt of *p*-chlorobenzoyl-acetoacetic ester is much facilitated. The quantities of the various substances used were as follows: acetoacetic ester, 37 g.; *p*-chlorobenzoyl chloride, 50 g. in 90 cc. of anhydrous ether; sodium, 13.12 g.; absolute alcohol, 200 cc. The yield of sodium salt was 90 g. This substance is of a yellow color, and much less soluble in water than the corresponding ortho compound.

One hundred and twenty grams of the sodium salt of *p*-chlorobenzoyl-acetoacetic ester were suspended in 600 cc. of water, 30 g. of ammonium chloride and 60 cc. of concentrated aqueous ammonia were added, and the mixture maintained at a temperature of 40–45° for 3 hrs., with continual shaking. The product was extracted with ether, the ethereal solution dried over calcium chloride, and the ether distilled. In this way the ester was obtained as a yellow, viscous oil, which, upon being cooled in a freezing

mixture, solidified to a mass of crystals. The crystals were freed from traces of adhering mother liquor by means of a porous plate, and then recrystallized from dilute alcohol.

p-Chlorobenzoylactic ester crystallizes in the form of colorless, flat prisms, and has a melting point of 38°. It is insoluble in water, readily soluble in alcohol, ether, benzene or ligroin.

0.4387 g. subs. gave 0.2880 g. AgCl. Calc. for $C_{11}H_{10}O_3Cl$: Cl, 15.67; found: 15.79.

Potassium Salt of *p*-Chlorobenzoylactic Ester.—Five grams of *p*-chlorobenzoylactic ester were treated with two equivalent weights of potassium hydroxide in 10% solution at the ordinary temperature. Upon stirring the mixture the potassium salt separated out as a white, voluminous mass, which was filtered off and recrystallized from absolute alcohol. The salt is slightly soluble in water, easily soluble in alcohol. It melts with decomposition at 265°.

0.2132 g. subs. gave 0.0682 g. K_2SO_4 . Calc. for $C_{11}H_{10}O_3ClK$: K, 14.37; found: 14.78.

***p*-Chlorobenzoylactic Acid.**—Three and one-half grams of *p*-chlorobenzoylactic ester were allowed to react with 2.4 g. (3 mols) of potassium hydroxide in 50 cc. of water at the ordinary temperature for a period of 3 days. At the end of this time the solution was filtered, and then extracted with ether in order to remove traces of unchanged ester and *p*-chloroacetophenone. From the cold solution the *p*-chlorobenzoylactic acid was precipitated by means of dilute sulfuric acid. The substance was recrystallized from a mixture of ether and ligroin.

p-Chlorobenzoylactic acid is very slightly soluble in water; slightly soluble in benzene or ligroin; readily soluble in alcohol or ether.

When heated gradually the substance decomposes into *p*-chloroacetophenone; but when quickly brought to a temperature in the vicinity of its melting point it melts at 232°.

0.0784 g. subs. gave 0.0568 g. AgCl. Calc. for $C_9H_7O_3Cl$: Cl, 17.88; found: 17.89.

Alkylation of *p*-Chlorobenzoylactic Ester.

Phenacyl *p*-Chlorobenzoylactic Ethyl Ester, $ClC_6H_4.CO.CH(CH_2.CO.C_6H_5).COOC_2H_5$.—To a solution of sodium ethylate, prepared from 2.05 g. of sodium and 35 cc. of absolute alcohol, 20 g. of *p*-chlorobenzoylactic ester were added. The solution of the sodium salt of *p*-chlorobenzoylactic ester was cooled, and then treated gradually with one equivalent weight (17.6 g.) of phenacyl bromide. The mixture became warm, and sodium bromide separated. The reaction was driven to completion by warming the contents of the flask on the water bath for fifteen minutes. Water was added to dissolve the sodium bromide, and the reddish oil which separated was taken up with ether. The ethereal solution was dried over calcium chloride, filtered, and the ether removed. The residual oil, after being allowed to remain in a cold place for several days, was

transformed into a crystalline mass. The crystals were pressed out on a porous plate, and then recrystallized from dilute alcohol. The yield was 50% of the theoretical.

Phenacyl *p*-chlorobenzoylactic ethyl ester crystallizes in the form of colorless prisms, and has a melting point of 63°. It is insoluble in water, slightly soluble in ligroin, fairly soluble in alcohol, readily soluble in ether, benzene or chloroform.

0.2238 g. subs. gave 0.1342 g. AgCl. Calc. for $C_{19}H_{17}O_4Cl$: Cl, 10.33; found: 10.36.

4-Chlorodiphenacyl, $C_6H_5.CO.CH_2.CH_2.CO.C_6H_4Cl$.—The ketonic decomposition of phenacyl *p*-chlorobenzoylactic ester, by means of dilute alkali, is not effected with the same smoothness as obtains in the case of the correspondingly substituted, nonhalogenated benzoylactic esters, the yield of ketone being diminished by the greater tendency of the former ester to undergo the acid decomposition.

Thirty-five grams of phenacyl *p*-chlorobenzoylactic ester were added to a solution of 13.6 g. of potassium hydroxide (2 mols) in a mixture of 300 cc. of water and 100 cc. of alcohol, and the solution boiled under a reflux condenser. After 2 hrs. boiling the contents of the flask were cooled, and the product filtered off. Several recrystallizations from alcohol, with the aid of bone black, gave a pure product, melting at 114.5°. The yield was poor.

4-Chlorodiphenacyl crystallizes in the form of colorless leaflets of pearly luster. It is insoluble in water, slightly soluble in ligroin, fairly soluble in alcohol or ether, readily soluble in benzene or chloroform.

0.3378 g. subs. gave 0.1814 g. AgCl. Calc. for $C_{18}H_{16}O_2Cl$: Cl, 13.02; found: 13.28.

***p*-Chlorophenacyl Benzoylactic Ester**, $C_6H_5.CO.CH(CH_2.CO.C_6H_4Cl).COOC_2H_5$.—This ester was prepared in order to determine the relative yields of 1,4-diketone produced in the saponification of this and of the isomeric ester described above.

Thirty-eight grams of *p*-chlorophenacyl bromide were added gradually to a solution of the sodium salt of benzoylactic ester, prepared from 3.65 g. of sodium, 80 cc. of absolute alcohol and 30 g. of benzoylactic ester. The reaction was completed by warming on the water bath for half an hour. The alcohol was distilled, and then water added to dissolve the sodium bromide. The oil which separated was extracted with ether, the ethereal solution dried over calcium chloride, and the greater part of the ether removed on the steam bath. In order to eliminate the last traces of ether the ester was placed *in vacuo* over sulfuric acid, a procedure which caused the transformation of the substance into a crystalline mass. The product was pressed out on a porous plate, and then recrystallized from alcohol. The yield was 75% of the theoretical.

p-Chlorophenacyl benzoylactic ester crystallizes in the form of colorless

² THIS JOURNAL, 31, 66 (1909).

sum of the molecular rotations of the two pentacetates (2B) is presumably equal to the sum of those of the two tetracetyl methylglucosides (2B), and this conclusion can be tested by experiment. Schliephacke¹ has calculated the data and finds that the sum is 39,700 for the pentacetates and 54,900 for the tetracetyl methylglucosides, the rotations of the four substances being measured in benzene solution. The disagreement is clear, and Schliephacke concludes that the foregoing theoretical views do not apply to the acetylated derivatives of glucose. In this connection, however, it is to be noticed that one of the four substances, namely, α -tetracetyl methyl glucoside, has been found by Moll van Charante² to form a crystalline compound with benzene and to have in benzene solution a specific rotation (173°) much larger than in alcoholic solution (137°). The corresponding beta form was found to have nearly identical rotations

TABLE I.—SPECIFIC ROTATIONS OF THE GLUCOSE PENTACETATES AND THE TETRACETYL METHYLGLUCOSIDES.

| Solvent. | Specific rotation. $[\alpha]_{\text{D}}^{20}$ Molecular rotation. ^a (Average.) | | | | Specific rotation. $[\alpha]_{\text{D}}^{20}$ Molecular rotation. ^a (Average.) | | | |
|---------------------------------|---|-----------|----------|----------|---|-----------|----------|----------|
| | Concentration. | Rotation. | Degrees. | Degrees. | Concentration. | Rotation. | Degrees. | Degrees. |
| Benzene..... | 5.302 | +20.51 | + 96.7 | | 5.061 | +0.45 | + 2.2 | ... |
| | 6.313 | +24.42 | + 96.7 | +37,800 | 6.544 | +0.71 | + 2.7 | ... |
| | 10.132 | +39.60 | + 97.7 | | 10.243 | +1.35 | + 3.3 | +1,100 |
| Chloroform..... | 5.252 | +21.35 | +101.6 | | 6.303 | +0.98 | + 3.9 | ... |
| | 6.738 | +27.38 | +101.6 | +39,600 | 6.801 | +1.04 | + 3.8 | +1,500 |
| | 10.906 | +44.36 | +101.7 | | 10.386 | +1.59 | + 3.8 | ... |
| Acetic ac. (99.5%).. | 6.325 | +27.48 | +108.6 | | 6.267 | +0.93 | + 3.7 | ... |
| | 10.399 | +45.24 | +108.8 | +42,400 | 10.621 | +1.87 | + 4.4 | +1,600 |
| Acetic ac. (50%).... | 3.919 | +16.95 | +108.1 | +42,200 | 3.641 | +0.47 | + 3.2 | +1,200 |
| Absolute alc..... | 0.5204 | + 2.1 | +100.9 | +39,400 | 0.5411 | +0.04 | + 1.9 | + 740 |
| Methyl alc..... | 1.4932 | + 6.25 | +104.6 | +40,800 | 1.2102 | +0.24 | + 4.9 | +1,900 |
| | α -Tetracetyl methylglucoside. | | | | β -Tetracetyl methylglucoside. | | | |
| Chloroform..... | 4.284 | +22.36 | +130.5 | | 3.813 | -2.78 | -18.2 | ... |
| | 8.178 | +42.72 | +130.6 | +47,300 | 8.0396 | -5.88 | -18.3 | -6,600 |
| Acetic ac. (99.5%).. | 1.690 | + 9.08 | +134.3 | | 4.359 | -3.40 | -19.5 | ... |
| | 3.769 | +20.16 | +133.7 | +48,500 | 8.544 | -6.66 | -19.5 | -7,100 |
| Acetic ac. (50%).... | 2.107 | +10.60 | +125.8 | | 3.757 | -3.34 | -22.2 | ... |
| | 3.882 | +19.76 | +127.2 | +45,800 | 8.002 | -7.28 | -22.7 | -8,130 |
| Methyl alc..... | 2.138 | +11.60 | +135.6 | +49,200 | 2.297 | -2.00 | -21.8 | -7,890 |
| Benzene ^c | 4.8166 | +33.84 | +175.5 | +63,530 | 4.6884 | -4.28 | -22.8 | -8,290 |
| Absolute alc ^b | 1.1736 | + 6.42 | +136.8 | +49,500 | 1.48 | -1.46 | -24.6 | -8,910 |

¹ *Ann.*, 377, 182 (1910).

² *Rec. trav. chim. Pays Bas*, 21, 42 (1902).

³ The molecular weights which are used are, 390 for glucose pentacetate and 362 for tetracetyl methylglucoside.

¹ Quoted from Koenigs and Knorr, *Ber.*, 34, 970 (1901).

^b Moll van Charante (*Loc. cit.*) found this value to be $[\alpha]_D^{20} = +137.3^\circ$.

in the two solvents.¹ It has seemed to us desirable to compare the rotations of the four substances in several solvents other than benzene since the relations seem to be complicated in the case of that solvent by the formation of a compound with one of the substances. The pentacetates of glucose and the tetracetates of methylglucoside were prepared as described in detail further on and the specific rotations of the pure substances were found to have the following values (Table I). The measurements refer to a temperature of 20°, sodium light, circular degrees of rotation, and the concentrations which are recorded signify the grams of substance which were contained in 100 cc. of solution, the weighings having been made in air with brass weights. The tube length in all cases is 4 decimeters. The chloroform used was *chloroformum purificatum*, U. S. P.

Tanret² has found for the specific rotation of α -glucose pentacetate the value +99° in benzene solution, 8 g. per 100 cc., and +101.7° in chloroform, 9 g. per 100 cc., and for the beta form of glucose pentacetate, he has found +2.8 in benzene, 8 g. per 100 cc., and +3.7 in chloroform, 14 g. per 100 cc. Our measurements confirm these values except in the case of the alpha form in benzene solution. Since we obtain for this substance in chloroform the same value as Tanret, it appears to us that his value in benzene must be high.

The data are now at hand for a comparison of the sums of the molecular rotations of the alpha and beta forms of glucose pentacetate and tetracetyl methylglucoside.

TABLE II.

Sum of the molecular rotations of the alpha and beta forms.

| Substance. | Chloroform. | Benzene. | Acetic acid. | | Absolute alcohol. | Absolute methyl alcohol. |
|---------------------------------|-------------|----------|--------------|--------|-------------------|--------------------------|
| | | | 99.5%. | 50%. | | |
| Glucose pentacetate.... | 41,100 | 38,900 | 44,000 | 43,400 | 40,100 | 42,700 |
| Tetracetyl methylglucoside..... | 40,700 | 55,240 | 41,400 | 37,700 | 40,600 | 41,300 |

The divergence of the sums for benzene solution has already been discussed. The difference in the values in 99.5% acetic acid is 2,600 in molecular rotation or approximately 7° in specific rotation, which seems larger than the uncertainty of the four measurements, and the divergence between the sums becomes greater when the proportion of water in the solvent is increased (50% acetic acid). In methyl alcoholic solution the sums differ only slightly beyond the limits of experimental error. The

¹ There is evidently a numerical error in Moll van Charante's calculation of the specific rotation of the β -form in alcohol from the measurements which he records, and, likewise, the value in benzene is incorrectly quoted from Koenigs and Knorr, but, nevertheless, the conclusion that the β -form has nearly identical rotations in benzene and alcohol is correct, according to our measurements in Table I.

² *Bull. soc. chim.*, 13, III, 261 (1895).

difference in chloroform solution is only 400 in molecular rotation or about 1° in specific rotation, which constitutes good agreement with the theory. The agreement between the sums in absolute alcoholic solution is also good.

Concerning the Rotatory Powers of the Two Octacetates of Cellose.—

The difference between the molecular rotations of the alpha and beta forms of glucose pentacetate is +38,100 in chloroform solution. According to the theory, the difference is the quantity $2A$, which should presumably have the same value for all the acetylated aldoses, in which the end asymmetric carbon atom is acetylated. The octacetate of cellose has been prepared in two crystalline forms, of specific rotation in chloroform solution +41° and -8°.¹ Assuming that these are the alpha and beta forms, respectively, their molecular difference ($2A$) becomes 33,200 which is smaller than the difference for the two pentacetates of glucose by 4,900 or approximately 7° in specific rotation, since the molecular weight of cellose octacetate is 678. The considerable divergence suggests that the α - and β -cellose octacetates may not yet have been obtained in a pure or fully separated condition.

Experimental.

Preparation of the α - and β -Pentacetates of Glucose and their Correlation with the Alpha and Beta Forms of Glucose.—The alpha and beta forms of glucose pentacetate have been correlated with the alpha and beta forms of glucose by the experiments of Behrend and Roth² in 1904 and of Behrend³ in 1907, which show that the acetylation of α -glucose in pyridine solution at zero degrees by the action of acetic anhydride yields α -pentacetate, while β -glucose, under the same conditions, gives rise to β -pentacetate. Recently, we have observed that a similar correlation may be obtained when glucose is acetylated with acetic anhydride and zinc chloride, provided the temperature is kept near zero. Before our experiments on this subject are described, it may be well to record the results which we obtained in repeating the work of Behrend and Roth, since our confirmatory data furnish a more nearly quantitative proof of the correlation in question.

Fifty grams of acetic anhydride were mixed with sixty-seven grams of commercial pyridine bases, the mixture cooled to 0° , 10 g. of pure crystalline α -glucose added and the mixture kept at 0° with occasional shaking during seven hours. The sugar had then dissolved completely. After standing seventeen hours longer at room temperature, the solution was poured into ice water and upon vigorous stirring the pentacetate crystallized in a few minutes. In three experiments, there were obtained from 10 g.

¹ Schliemann, *Ann.*, 378, 372 and 374 (1911).

² *Ann.*, 231, 369 (1904).

³ *Ibid.*, 353, 109 (1907).

of α -glucose 19.0, 19.5 and 18.5 g. of pentacetate with specific rotations in chloroform solution of 91.3° , 90.9° and 92.1° . The weight of pentacetate which is the equivalent of 10 g. of glucose is 21.7 g.

In another experiment, the same quantities of α -glucose, acetic anhydride and pyridine were kept at 0° for 24 hrs. There were obtained 19.8 g. of pentacetate with a specific rotation of 94° in chloroform. Since the specific rotation of pure α -glucose pentacetate in chloroform is about 101.6° , while that of the beta is only 3.9° , it is evident that the crystalline product consisted largely of the alpha isomer.

β -Glucose acetylates more readily than the alpha isomer. The β -glucose used had a specific rotation of $20-21^\circ$. With the same amounts of sugar, acetic anhydride and pyridine as were used in acetylating α -glucose, there were crystallized after acetylation at 0° during 3, 5, 6 and 24 hours, respectively, 14, 18, 19.5 and 20.5 g. of pentacetate of specific rotations varying between $+5.5$ and $+5.8$ in chloroform. It is evident that the product was almost wholly β -pentacetate.

It was found that powdered glucose can be acetylated readily at 0° by a solution of zinc chloride in acetic anhydride. Four grams of fused zinc chloride were dissolved in 40 g. acetic anhydride, the solution was cooled to 0° , 10 g. of pure α -glucose were added, a little at a time, and the mixture was kept at zero with an occasional shaking for five hours. During this time most of the sugar dissolved but there remained some which had not been attacked; the weight of this portion, after filtering it off, was found to be 2.85 g. The filtrate crystallized in a few minutes after falling into water and yielded 7.15 g. of dry pentacetate, of specific rotation 92° in benzene. The water from which these crystals were obtained was then shaken out with chloroform, and by evaporating the chloroform solution nearly to dryness and pouring it again into water, a second lot of crystalline pentacetate was obtained, showing a specific rotation of 86° and weighing 3.64 g. when dry. An extraction of the second water with chloroform yielded 2.26 g. of a very viscous sirup which did not crystallize. Summing up these weights, there were obtained 13.05 g. of acetylated material from 7.15 g. of sugar, the latter being equivalent by theory to 15.44 g. pentacetate. Since the specific rotation of α -glucose pentacetate in benzene is about 96.7° , while that of the β -pentacetate in benzene is only 2.7° , it is evident that the crystalline product consisted largely of the alpha isomer.

In a second similar experiment, the time of reaction was increased to 45 hours with the result that only 0.33 g. glucose remained undissolved. There were obtained 15.20 g. of pentacetate of specific rotation 78° , 3.03 g. of 59° , and 1.30 g. of sirupy residue, making 19.53 g. of acetylated product against 19.89 g. of pentacetate by theory. There is evidence from the rotatory powers of the crystals that a partial change of the α .

pentacetate to the β form took place during the prolonged time of the reaction; this change is just detectable in the first experiment. It has been found during numerous preparations of this substance that 10 g. of pure α -glucose will yield under constant stirring of the acetylation mixture for 8 hours about 13 g. of pentacetate of specific rotation 83° , from which the pure α form may be readily obtained by the usual recrystallization from alcohol.

With the same proportions of sugar, zinc chloride and acetic anhydride that are recorded in the experiments just mentioned, 10 g. of crystalline β -glucose, of specific rotation 21° , after 5 hours' reaction at 0° , yielded 2.73 g. undissolved sugar, 10.75 g. pentacetate of rotation 8.7° , 2.22 g. of 18° , and 1.06 g. of viscous sirup, making a total of 14.03 g. of acetylated product against 15.75 g. of pentacetate by theory. The crystals from this experiment yielded pure β -pentacetate on recrystallization. In a second similar experiment the time of reaction was extended to 24 hours and there were found 0.43 g. sugar remaining undissolved, 15.10 grams pentacetate of rotation 14° , 3.43 g. of rotation 43° , and 1.20 g. of sirup, making 19.73 g. of acetylated product against 20.73 g. pentacetate by theory. It is again noticeable from the rotations of the product that the longer duration of the reaction causes isomeric change, in this instance transforming some of the β -pentacetate into the alpha form. It has been found that 10 g. of crystalline β -glucose will yield, with eight hours' stirring in the acetylation mixture, about 17 g. of pentacetate of specific rotation 17° , from which the pure β -pentacetate may be readily obtained by recrystallization from alcohol.

These acetylations of α - and β -glucose, with acetic anhydride and zinc chloride, correlate these substances with the α - and β -pentacetates of glucose, respectively, and confirm the similar correlation by Behrend, who used pyridine as the catalyst.

The purification of the samples of the pentacetates which were used in making the measurements recorded in Table I was accomplished by recrystallizing from 95% alcohol until the rotation became constant. The crystals were dried by raising the temperature gradually to 100° . The pure alpha pentacetate melted at $112-113^\circ$, corrected.

Two acetyl estimations made by boiling in a quartz flask with reflux condenser 0.5 g. of pentacetate with 90 cc. of 0.3 *N* sulfuric acid during three hours gave 76.73% and 76.97% acetic acid; calc. 76.93%.

The pure beta pentacetate melted at 132° , corrected, and yielded 77.16% acetic acid after hydrolysis. Both pentacetates were found to yield the theoretical amount of glucose after the hydrolysis of 5 g. of pentacetate with 50 cc. of 5% sulfuric acid during two hours on the steam bath, the estimation of the glucose being taken from a measurement of the rotation of the hydrolyzed solution.

Preparation of α -Tetracetyl Methyl Glucoside.—This substance was prepared by acetylating α -methylglucoside with acetic anhydride and sodium acetate, according to the directions of Koenigs and Knorr.¹ It was recrystallized from 95% alcohol until a constant specific rotation was obtained. It melted at 100–101° corrected.

Preparation of β -Tetracetyl Methylglucoside.—This compound has been prepared by Koenigs and Knorr² from β -bromoacetyl glucose and from β -acetonitroglucose, and Moll van Charante³ has prepared it from β -methylglucoside. We followed Koenigs and Knorr's procedure slightly modified, using β -bromoacetyl glucose. Twenty-five g. of β -bromoacetyl glucose were dissolved in 200 cc. methyl alcohol. To this were added 12.5 g. silver nitrate dissolved in 200 cc. methyl alcohol and 50 cc. water. The filtrate from the silver bromide precipitate was treated with hydrogen sulfide and then shaken with barium carbonate. The filtrate from this was evaporated to a thick syrup on the steam bath under diminished pressure. On cooling, it crystallized to an almost solid mass. It was recrystallized from absolute methyl alcohol until the specific rotation was constant. The yield was 13.5 g., having a melting point of 104–105° (corr.).

THE ISOMERIC OCTACETATES OF LACTOSE.

By C. S. HUDSON AND J. M. JOHNSON.⁴

Received March 5, 1915.

Schutzenberger and Naudin⁵ acetylated lactose by boiling it with acetic anhydride but did not obtain a crystalline product. Herzfeld⁶ crystallized lactose octacetate by acetylating the sugar with acetic anhydride and anhydrous sodium acetate (the Liebermann⁷ method), and found the substance to melt at 86°, but did not learn its rotatory power. Schmöger⁸ prepared the octacetate by this method, reported a higher melting point, 95–100°, and observed a specific rotation of -3.5° in chloroform. Fischer and Armstrong⁹ found this octacetate to melt at 106°.

¹ *Ber.*, 34, 970 (1901).

² *Loc. cit.*, 969 and 977.

³ *Loc. cit.*

⁴ Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture. A preliminary notice was read at the Cincinnati meeting of the American Chemical Society, April, 1914. The authors desire to express their appreciation of the valuable services of Mr. A. S. Eastman, who has repeated during the summer of 1914 the preparation of the new octacetyl lactose. The data of the present article are partly taken from his work.

⁵ *Bull. soc. chim.*, II, 12, 208 (1869).

⁶ *Ber.*, 13, 265 (1880).

⁷ *Ibid.*, 11, 1619 (1878).

⁸ *Ibid.*, 23, 1452 (1892).

⁹ *Ibid.*, 35, 841 (1902).

regarded it as a mixture of two isomers, but were unable to separate it into its assumed components.

We attempted to prepare crystalline lactose octacetate by the methods which have been described by these different authors, and also by the method which Kremann¹ has used, but the products did not crystallize. Finally, a method was devised by which the octacetate may be readily prepared in crystals.

Four hundred cc. of acetic anhydride were heated to 100° in a flask of several liters' capacity and 25 g. of anhydrous sodium acetate were added. The mixture was heated nearly to the boiling point of the solution and there was added to it, a little at a time, 100 g. of commercial milk sugar, which consists principally of the monohydrated alpha form of lactose. After a small amount of the sugar had been added, a vigorous reaction began, accompanied by boiling of the acetic anhydride. The gas flame under the flask was then turned off and the addition of the sugar continued, a small amount at a time, until all was in solution, the reaction furnishing enough heat to keep the acetylation going to completion. After all the lactose had dissolved, the solution was boiled for ten minutes and poured into a large volume of cold water. The insoluble viscous mass which precipitated was stirred with the water, allowed to settle, the water poured off and fresh water added from time to time. After standing over night under water, the mass solidified and was broken up with a rod. It was then filtered on a Buchner funnel, washed well with water and dried in the air. The product was ground, and extracted with warm ether by decantation until all ether-soluble material was removed. The residue, which was by far the larger portion of the product, was then dried from all ether and dissolved in hot 95% alcohol. On cooling and stirring frequently, a spontaneous crystallization was invariably obtained. The compound may also be recrystallized from chloroform by the addition of alcohol or ether, or from benzene by adding ether. The recrystallization from alcohol was repeated until a constant value for the specific rotation was obtained, and the yield of the purified product was about 55% of the theoretical.

The rotatory power of this octacetate in chloroform solution is to the left, and our measurements (see Table I) on the carefully purified material show that the concentration influences the specific rotation appreciably. Schmöger's value comes within the range of our results, but the concentration of his solution is not recorded.

The melting phenomena which are exhibited by the substance are peculiar, as is to be expected from the fact that observers have obtained melting points as far apart as 86° (Herzfeld) and 106° (Fischer and Armstrong). In our first observations on the carefully purified and dried

¹ *Monatsh.*, 23, 483 (1902).

octacetate, the microscopic crystals appeared to melt from 95° to 99° , but it was noticed that the mass kept a white appearance to 104° . This behavior was understood when the crystals were observed under magnification during the process of melting, because it was then seen that each crystal distinctly melted at about 90° , but the melt is so viscous at that temperature that the drops do not coalesce, or only very slowly. When they do unite, as the temperature rises toward 100° , air bubbles are included in the melt and give it a white appearance which vanishes as the viscous liquid becomes more fluid at or about 104° . We regard this lactose octacetate, therefore, as melting at about 90° , and fairly sharply, considering that the melt is very viscous and the heat transfer slow in consequence.

For analysis; the material was dried in a vacuum oven at 70° to constant weight. 0.6792 and 0.5513 g. subs. gave 1.2241 and 0.9951 g. CO_2 and 0.3454 and 0.2808 g. H_2O . Found: 49.16% and 49.23% C; 5.70% and 5.71% H; calc. for $\text{C}_{17}\text{H}_{14}\text{O}_{11}(\text{CH}_3\text{CO})_8$: 49.54% C and 5.65% H.

The acetyl percentage was measured by boiling 0.5 g. samples with 50 cc. of *N*/3 sulfuric acid under a reflux condenser for three hours, and titrating with 0.1 *N* sodium hydroxide solution, using phenolphthalein as indicator. The reliability of the method was tested in numerous blank determinations, both with and without the addition of lactose. By varying the time of hydrolysis, the latter was shown to be complete in three hours. Using 0.5 g. samples, the percentages of acetyl (CH_3CO) found in two experiments were 50.75 and 50.71 while the theory requires 50.74%.

Preparation of an Isomeric Crystalline Octacetate of Lactose.—When lactose octacetate of m. p. 90° was dissolved in glacial acetic acid containing a small amount of zinc chloride, there was observed at 20° a slow change of rotation day by day to the right. The speed of this change could be hastened by heating the solution on the steam bath. A similar change of rotation towards the right was observed when acetic anhydride containing zinc chloride was used as the solvent, and in this case a new crystalline product was isolated by the following procedure:

Fifty grams of lactose octacetate (m. p. 90°) and 5 g. of fused zinc chloride were dissolved by warming in 250 cc. acetic anhydride, and then heated thirty minutes on the steam bath. The mixture was cooled, poured into a large volume of cold water and allowed to stand under the water over night. The hard mass was filtered off, ground in a mortar, dried in the air, and dissolved in ether. With an occasional scratching of the glass vessel the ether solution was brought to crystallization after a day or so at 20° . These crystals were then recrystallized from 95% alcohol, at first with some difficulty, but after several recrystallizations with ease. A yield of 56% was obtained. A compound differing from the original octacetyl lactose in many physical properties was thus prepared. It melts sharply at 152° , consists of fine felted needles, is more soluble in ether and in alcohol than the parent substance and, like the latter, is very

soluble in chloroform, benzene and ethyl acetate, difficultly soluble in water and almost insoluble in petroleum ether. Determination of the acetyl value, elementary analysis, and the regeneration of lactose showed this compound to be an octacetyl lactose. Milk sugar was regenerated from it by pouring cold alcoholic potash on a suspension of the substance in alcohol, filtering off the lactose, recrystallizing, and identifying the sugar by its cupric reducing power, its specific rotation, its solubilities and its failure to ferment with yeast.

0.3202 and 0.4732 g. subs. gave 0.5810 and 0.8573 g. CO_2 , and 0.1626 and 0.2372 g. H_2O . Found: 49.49% and 49.41% C; 5.69% and 5.62% H.

Calc. for $\text{C}_{12}\text{H}_{14}\text{O}_{11}(\text{CH}_3\text{CO})_8$: 49.54% C and 5.65% H.

The acetyl percentage, estimated as previously described, showed 50.84% and 50.66% CH_3CO ; calc.: 50.74%.

This isomeric octacetyl lactose is also formed in small amount along with the earlier discovered octacetate during the acetylation of lactose with acetic anhydride and anhydrous sodium acetate. We obtained a small quantity of the new isomer in crystals from the ether extraction which has been mentioned in connection with the description of the preparation of octacetyl lactose of m. p. 90° .

Determinations of the specific rotation of the new isomeric octacetyl lactose are recorded in Table I and show that the substance is strongly dextrorotatory, distinguishing it from the earlier discovered lactose octacetate which is levorotatory.

TABLE I.—THE SPECIFIC ROTATIONS OF THE TWO LACTOSE OCTACETATES.

| Solvent. | Conc. g. per 100 cc. of solution. | | | Length of tube. | Reading. | $[\alpha]_D^{20}$. Old isomer or β -octacetate. M. p. 90° . | $[\alpha]_D^{20}$. New isomer or α -octacetate. M. p. 152° . | Conc. g. per 100 cc. of solution. | | | Length of tube. | Reading. | $[\alpha]_D^{20}$. New isomer or α -octacetate. M. p. 152° . |
|------------------------------|-----------------------------------|----------|--------------------------|-----------------|----------|--|--|-----------------------------------|----------|----------|-----------------|----------|--|
| | Dm. | Degrees. | Degrees. | | | | | Dm. | Degrees. | Degrees. | | | |
| Chloroform ¹ | 10.3644 | 4 | — 1.95 Ang. | — 4.70 | 7.8560 | 4 | +16.85 Ang. | +53.62 | | | | | |
| Chloroform ¹ | 10.6512 | 2 | — 2.69 V. ² | — 4.37 | 10.1592 | 2 | +31.44 V. | +53.54 | | | | | |
| Chloroform ¹ | 10.7344 | 2 | — 2.62 V. | — 4.22 | 10.3746 | 4 | +22.05 Ang. | +53.13 | | | | | |
| Chloroform ¹ | 10.8448 | 2 | — 2.80 V. | — 4.47 | 10.6016 | 2 | +11.51 Ang. | +54.28 | | | | | |
| Chloroform ¹ | 19.4414 | 4 | — 2.75 Ang. | — 3.54 | 20.3340 | 4 | +44.55 Ang. | +54.77 | | | | | |
| Benzene..... | 5.72 | 4 | — 5.90 Ang. | —25.78 | 10.66 | 4 | +35.2 V. | +28.6 | | | | | |
| Benzene..... | 10.49 | 4 | — 9.87 Ang. | —23.52 | 10.3044 | 2 | + 5.90 Ang. | +28.6 | | | | | |
| Benzene..... | 9.8874 | 4 | —27.31 V. | —23.90 | 10.57 | 4 | +12.08 Ang. | +28.57 | | | | | |
| Benzene..... | | | | | 5.8456 | 2 | + 8.43 V. | +24.95 | | | | | |
| Benzene..... | | | | | 5.21 | 4 | + 5.17 Ang. | +24.81 | | | | | |
| Benzene..... | | | | | 4.7518 | 4 | + 4.54 Ang. | +23.89 | | | | | |
| Glacial acetic acid..... | 10.3014 | 4 | No rotation ³ | | 9.8868 | 2 | +11.85 Ang. | +59.93 | | | | | |
| | | | | | 10.36 | 4 | +71.7 V. | +59.87 | | | | | |
| | | | | | 6.0932 | 2 | + 7.40 Ang. | +60.72 | | | | | |
| 50% acetic acid | 10.0 | 2 | No rotation | | 4.9356 | 2 | + 6.06 Ang. | +61.40 | | | | | |

¹ The chloroform used was chloroformum purificatum, U. S. P.

² 1° Veritzke = 0.346° Angular.

³ None could be observed and the limit of detection was somewhat less than 0.05° V.

The Equilibrium between the Two Isomeric Octacetates.—Two and one-half grams of the older isomer were dissolved in glacial acetic acid containing zinc chloride, the solution was made up to 50 cc. and allowed to stand at 20° during five months. There was a slow change in the rotation as read in a 200 mm. tube with a Ventzke instrument from +0.7° to +15.3°. A corresponding solution of the new isomer changed in rotation during the same time from +17.6° to +15.2°. Equilibrium was thus reached between the two forms in glacial acetic acid under the specified conditions when about 86% of the new isomer was present.

Five grams of the older isomer and 0.5 g. ZnCl_2 when made up to 50 cc. with acetic anhydride at 20° gave a specific rotation of +4.3°. This solution was heated at 100° for 30 minutes, cooled to 20° and the specific rotation was found to be +51.9°, and the value was not changed by a further heating for ten minutes. Five grams of the new isomer were treated in the same manner and the specific rotation was found to change from +64.0° to +52.8°, at which value it became constant. The point of equilibrium at 100° is then about +52°, which shows that about 81% of the new isomer is present in the equilibrium mixture in acetic anhydride.

Preparation of Bromoacetyl Lactose from the New Lactose Octacetate.

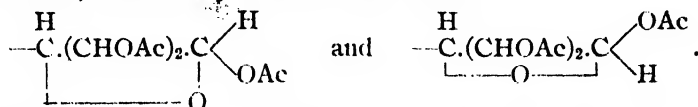
—Five grams of lactose octacetate of specific rotation -4° were dissolved in 7 cc. warm acetic anhydride, the mixture cooled, 7 cc. acetic acid saturated with hydrobromic acid gas were added, and the solution kept at room temperature until its polariscopic reading became constant, which required about forty minutes. The solution was then poured into ice water and treated according to Fischer's¹ directions for the preparation of heptacetyl bromolactose. We obtained 3 g. of recrystallized substance of m. p. 139–141°, and specific rotation +105° in chloroform, which was evidently identical with Fischer's preparation which melted at 141–142° and had a specific rotation in chloroform of +104.9°. When the new lactose octacetate of specific rotation +53° was treated by the same procedure, there were obtained 2 g. of recrystallized substance melting at 139–141° and having a specific rotation of +104° in chloroform solution. From the two lactose octacetates, therefore, the same heptacetyl bromolactose was obtained.

Molecular Weights of the Isomeric Octacetates in Benzene.—The freezing temperatures of solutions of the new isomeric octacetate containing per hundred grams of benzene 1.34, 1.58, and 3.38 g. substance, respectively, were found to be 0.099°, 0.113°, and 0.242° below that of the solvent, indicating on an average the molecular weight of 692, in comparison with the theoretical value 678. The freezing-point depressions of solutions of the earlier discovered octacetate gave the value 611.

The Structural Formulas and Nomenclature of the Isomeric Oct-

¹ *Ber.*, 43, 2530 (1910).

acetates.—The existence of isomeric pairs of the fully acetylated derivatives of all the aldose and ketose sugars, corresponding to the well-known α and β forms of glucose pentacetate and of cellose octacetate, respectively, is to be expected. The isomerism of the two lactose octacetates presumably depends upon the space arrangement about the terminal asymmetric carbon atom, which may take the two forms



On this view, the two lactose octacetates are the derivatives, respectively, of the well-known α and β forms of lactose, and the octacetate of stronger dextro rotation, which is the new isomer, is to be named in accordance with the naming of the forms of lactose, the α form, the older isomeric octacetate being the β form. This naming of the octacetates is supported by the following comparison of their rotatory powers with those of the α and β forms of glucose pentacetate, since the α - and β -pentacetates have been correlated with the α and β forms of glucose by the experiments of Behrend and Roth. Writing the molecular rotations¹ of α - and β -glucose pentacetates as $(A + B)$ and $(-A + B)$, respectively, the molecular rotations of the corresponding α - and β -octacetates of lactose may be written $(A + B')$ and $(-A + B')$, respectively. It follows that the difference of the molecular rotations of the first pair of substances ($2A$) is equal to that of the second pair, a conclusion which may be tested experimentally from the data recorded in Table II.

The differences of the molecular rotations of the α - and β -glucose pentacetates in several solvents are quoted from the foregoing article by Hudson and Dale, and those of the α - and β -lactose octacetates are obtained from the averaged values of Table I, multiplied by 678, the molecular weight of the octacetate.

TABLE II.
Difference of the molecular rotations of the α and β forms.

| Substance. | Chloroform. | Benzene. | Acetic acid. | |
|--------------------------|-------------|----------|--------------|--------|
| | | | 99.5%. | 50%. |
| Glucose pentacetate..... | 38,100 | 36,700 | 40,800 | 41,000 |
| Lactose octacetate..... | 39,400 | 34,300 | 40,600 | 41,600 |

The numbers agree closely in the two strengths of acetic acid and also the agreement in chloroform solution is a satisfactory one, since the difference between the two values corresponds to less than 2° in specific rotation. The values in benzene solution are farther apart, and confirm Hudson and Dale's conclusion that benzene is not a suitable solvent for such comparisons.

WASHINGTON, D. C.

¹ For the meaning of this formulation, see THIS JOURNAL, 31, 66 (1909)

THE ISOMERIC ALPHA AND BETA OCTACETATES OF MALTOSÉ AND OF CELLOSE.

By C. S. HUDSON AND J. M. JOHNSON.¹

Received March 12, 1915.

In continuation of the work which we recently described² regarding the preparation of the new alpha lactose octacetate by heating the well-known beta octacetate in acetic anhydride solution with a small amount of zinc chloride, we have applied the method to the octacetate of maltose which is described in the literature and have transformed it likewise to an isomeric crystalline octacetate. The new maltose octacetate rotates to the right in chloroform solution $+122^\circ$, in comparison with the value $+63^\circ$ for the octacetate from which it was prepared, and on this account we have chosen to designate the new substance as the alpha form, and the earlier discovered octacetate as the beta isomer.

Preparation of β -Maltose Octacetate.—By acetylating maltose with acetic anhydride and sodium acetate, Herzfeld³ first prepared crystals of this substance, but the earliest accurate description of it was given some years later by Ling and Baker,⁴ who found it to melt at $158-9^\circ$, and to show a specific rotation of $+62$ in chloroform solution. We prepared from pure maltose without difficulty a considerable quantity of this octacetate by the Liebermann method and recrystallized it until the specific rotation became constant. The substance melted at $159-60^\circ$ corr. and exhibited the specific rotations which are recorded in a part of Table I.

Preparation and Description of the New Isomeric α -Maltose Octacetate.—One hundred grams of β -maltose octacetate, of m. p. 159° , were dissolved in 250 cc. of acetic anhydride containing 5 g. of zinc chloride, and the solution was heated on the steam bath until its rotation became constant, which required about eleven minutes only. During this heating the specific rotation changed from the initial value of $+59.8^\circ$ to $+110.4^\circ$, and it was concluded that this large increase in dextrorotation indicated that most of the original β -octacetate had changed to the hypothetical alpha form. Repeated attempts were made to crystallize the new isomer and this was at last accomplished by the following procedure: The solution which had reached constant rotation was poured into cold water and allowed to stand with an occasional renewal of the water until the viscous insoluble mass of acetylated sugar became hard. After drying and powdering the solid mass, it was dissolved in a very small amount of 95% alcohol so as to form a thick sirup. After standing for some weeks

¹ Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

² THIS JOURNAL, 37, 1270 (1915).

³ Ber., 13, 267 (1880); Ann., 220, 215 (1883).

⁴ J. Chem. Soc., 67, 212 (1895); Ber., 28, 1019 (1895); cf. Herzfeld, *Ibid.*, 28, 440 (1895).

at room temperature, this sirup crystallized and by seeding with this material freshly prepared sirups could be brought to rapid crystallization. The new compound was recrystallized from alcohol until the rotatory power reached a constant value. The pure crystals melted at 125° corr. after thorough drying at 70° in a vacuum oven.

0.2112 and 0.2073 g. subs. yielded 0.3832 and 0.3755 g. CO_2 , and 0.1098 and 0.1065 g. H_2O , corresponding to 49.54 and 49.40% C, 5.82 and 5.75% H, respectively. Calc. for maltose octacetate: 49.54% C and 5.65% H.

An acetyl estimation was made by boiling in a quartz flask with reflux quartz condenser 0.5 g. substance with 100 cc. 0.25 *N* sulfuric acid during six hours and it indicated 50.62% acetyl (CH_3CO), and duplicate experiments in which the boiling lasted only three hours gave 50.68 and 50.72% acetyl, respectively. These three values agree with the theoretical 50.74% for a maltose octacetate.

The molecular weight of the compound was determined from the lowering of the freezing point of its solutions in benzene. Six experiments with different concentrations showed depressions between 0.090 and 0.235° , which indicated values for the molecular weight ranging between 664 and 694, in comparison with 678, the theoretical value for maltose octacetate. Ling and Baker (*l. c.*) have found 633 in a measurement of the molecular weight of β -maltose octacetate in benzene by the freezing-point method.

Table I records the specific rotatory power of the new octacetate in several solvents, in comparison with the rotation of the β -octacetate. The tube length in all cases is 4 dcm., the readings are expressed in circular degrees for sodium light, and the concentration in grams per 100 cc. of solution, the weighings being made in air with brass weights. The chloroform used was *chloroformum purificatum*, U. S. P.

TABLE I.—THE SPECIFIC ROTATIONS OF THE MALTOSE OCTACETATES.

| Substance. | Solvent. | Concentration. | Reading. | $[\alpha]_D^{20}$. |
|------------------------------|-------------------|----------------|----------|---------------------|
| α -Maltose octacetate | Chloroform | 5.01 | +24.60 | +122.77 |
| | Chloroform | 9.94 | +48.50 | +121.94 |
| | Benzene | 5.00 | +24.80 | +124.05 |
| | Benzene | 9.93 | +48.90 | +123.11 |
| | 99.5% acetic acid | 3.95 | +19.63 | +124.30 |
| | 99.5% acetic acid | 10.12 | +50.30 | +124.25 |
| | Methyl alcohol | 5.06 | +24.55 | +121.24 |
| | Methyl alcohol | 10.07 | +48.43 | +120.25 |
| β -Maltose octacetate | Chloroform | 5.09 | +12.75 | + 62.59 |
| | Chloroform | 10.61 | +26.95 | + 62.91 |
| | Benzene | 5.20 | +15.55 | + 74.83 |
| | Benzene | 10.26 | +30.70 | + 74.52 |
| | 99.5% acetic acid | 5.45 | +11.95 | + 54.80 |
| | 99.5% acetic acid | 10.43 | +23.95 | + 57.40 |

The Rotatory Powers of the Alpha and Beta Forms of Cellose Octacetate.—It has been mentioned by Hudson and Dale¹ that the difference between the molecular rotations of the two isomeric octacetates of cellose as given in the literature does not accord with the difference for the two

¹ THIS JOURNAL, 37, 1264 (1915).

glucose pentacetates. We have investigated this disagreement and find that the recorded value of the specific rotation of β -cellose octacetate is too small and that the correct values for the two octacetates agree well with those of the glucose pentacetates. Skraup and Geinsperger¹ found the specific rotation of α -cellose octacetate to be $+43.6$ and the value -30 was found for the beta form, both in chloroform solution. Hardt-Stremayr² working later in the same laboratory, found $+42.7^\circ$ and $+42.9^\circ$ for the alpha octacetate in chloroform, and expressed the opinion³ that Geinsperger's value -30 should read $+30$ and that it really referred to an impure sample of the alpha form. Schliemann⁴ has purified the alpha form by numerous recrystallizations from alcohol and from benzene and has found the value $+41.5$ for its rotation. He found the value -8° for the β -octacetate in chloroform.

We have prepared α -cellose octacetate by the usual method of treating filter paper with acetic anhydride and a small amount of concentrated sulfuric acid. The acetate was recrystallized from hot 95% alcohol until the specific rotation became constant and the following values were found: 9.85 g. per 100 cc. in chloroform $[\alpha]_D^{20} = +41.95^\circ$, 5.85 g. per 100 cc., $+40.87^\circ$, the chloroform used being *chloroformum purificatum*, U. S. P. The melting point of the compound was 229.5° corr. From this acetate cellose was regenerated by saponification with alcoholic potash, and the crystalline sugar was then acetylated with acetic anhydride in the presence of anhydrous sodium acetate. The product was poured into cold water and soon crystallized. It was found that sixteen successive recrystallizations, first from alcohol and then from mixtures of chloroform and alcohol and of chloroform and ether, were required in order to fully purify the octacetate and obtain material which did not change in rotatory power after further recrystallization. From 75 g. of cellose, 111 g. of octacetate were obtained as the first product. Its rotation was -7.5° in chloroform, which agrees with Schliemann's observation. After the sixteen recrystallizations, 19 g. of pure material, of melting point 202° corr., were in hand. 10.88 g. of this β -octacetate per 100 cc. of its chloroform (*chloroformum purificatum*, U. S. P.) solution rotated to the left, $[\alpha]_D^{20} = -14.48$, and 5.10 g. per 100 cc. gave the value -14.74° .

Transformation of β -Cellose Octacetate to the Alpha Isomer.—Maquenne and Goodwin⁵ mention that β -cellose octacetate can be changed to the alpha isomer by heating in acetic anhydride solution with a small quantity of sulfuric acid. We have carried out this transformation by

¹ *Monatsh.*, 26, 1471 (1905).

² *Ibid.*, 28, 73 (1907).

³ *Loc. cit.*, p. 68.

⁴ *Ann.*, 378, 366 (1910).

⁵ *Bull. soc. chim.*, [3] 31, 856 (1904).

heating an acetic anhydride solution of the beta form with a small amount of zinc chloride. 2.96 g. of the β -acetate dissolved in the cold in 50 cc. acetic anhydride containing a trace of zinc chloride read $[\alpha]_D^{20} = -4.8^\circ$, and after fifteen minutes' heating on the steam bath, its rotation became constant at $+44.9^\circ$. From this solution, by pouring into water and recrystallizing, there were obtained 1.9 g. of α -cellose octacetate of m. p. $221-3^\circ$ and specific rotation $+40.5$ in chloroform. Likewise, the beta form was transferred to the alpha by heating with acetic anhydride containing some sulfuric acid, as mentioned by Maquenne and Goodwin, but the yield was very much smaller, due probably to the hydrolyzing action of the acid. Hardt-Stremayr¹ sought to transform the α -octacetate to the beta by the same methods but without success. Evidently the equilibrium in acetic anhydride solution between the two isomers is so far towards the side of the alpha form that it alone has been obtained from the mixture. The recorded rotatory power of the transformed solution also indicates that the point of equilibrium is far towards the side of the α -octacetate. This transformation of the β - to the α -octacetate makes it clear that the production of α -cellose octacetate by the acetolysis² of cellulose with acetic anhydride and sulfuric acid does not throw any light upon the question whether cellulose is a condensation product from α -cellose or β -cellose, because either form of the sugar must yield the same α -octacetate in the presence of the reagent mentioned.

Comparison of the Rotations of the Pentacetates of Glucose and the Octacetates of Lactose, Maltose and Cellose.—We have previously shown that the difference between the molecular rotations of the α - and β -glucose pentacetates in chloroform solution agrees with the difference for the α - and β -lactose octacetates, as is suggested by theoretical considerations. The data are now at hand for an extension of this comparison to the octacetates of maltose and of cellose. Since these have the same molecular weight as lactose octacetate, it is sufficient to compare the specific rotations of the substances. In chloroform solution α - and β -lactose octacetates rotate $+53$ and -4 , respectively, the difference being 57° , α - and β -maltose octacetates rotate $+122^\circ$ and $+63^\circ$, with a difference of 59° , and α - and β -cellose octacetates rotate $+41$ and -15 , giving the difference 56° . These differences agree closely and also, as may be understood from what precedes, agree with the value which can be calculated from the observed difference between the rotations of the α - and β -glucose pentacetates, which have the values $+102$ and $+4$, respectively. Their specific rotation difference is thus 98° and since their molecular weight

¹ *Loc. cit.*

² The term acetolysis is coming into use to designate the splitting and simultaneous acetylation of polysaccharides, in the same sense that hydrolysis indicates the splitting and simultaneous hydration.

is 390, in comparison with 678 for the biose octacetates, the calculated difference for the latter becomes $98 \times (390/678) = 56^\circ$. As has been shown from theory, the value of this difference is a measure of the rotatory power of that end asymmetric carbon atom which is common to all the acetylated aldose sugars. The close numerical agreement, among the four acetylated sugars here described, may be interpreted to mean that the differences in structure which distinguish them do not appreciably affect the rotatory power of this end asymmetric carbon atom. Possibly this may be due somewhat to the fact that the three bioses are derivatives of glucose, and have much of their structure in common with that sugar.¹

WASHINGTON, D. C.

THE ISOMERIC PENTACETATES OF MANNOSE.

By C. S. HUDSON AND J. K. DALE.²

Received March 12, 1915.

The possibility of the existence of two isomeric pentacetates of *d*-mannose has been foreshadowed by Franchimont's³ recognition of the two pentacetates of glucose, the beta form of which was discovered by him⁴ in 1879 and the alpha form by Erwig and Koenigs⁵ in 1889. Mannose may be readily acetylated by any of the customary reagents but it is only within the last two years that methods have been applied which result in a crystallization of the acetylated sugar. E. Fischer and Oetker⁶ have prepared crystalline mannose pentacetate by acetylating β -mannose at low temperature (0°) with a mixture of acetic anhydride and pyridine (Behrend's method), and have regarded the substance, which they found to melt at 117.5° and to have a specific rotation of -24.9 in chloroform solution, as the β -pentacetate because of its preparation from β -mannose by the above mentioned method and its levorotation. Shortly before the appearance of Fischer and Oetker's description of the β -pentacetate, our colleague, Mr. H. L. Sawyer, succeeded in crystallizing from the products of the action of acetic anhydride and zinc chloride on β -mannose at 0° a mannose pentacetate which he found to melt at $117-118^\circ$ and

¹ The transformation of galactose pentacetate of m. p. 142° by heating with acetic anhydride and zinc chloride has yielded an isomeric crystalline pentacetate, of m. p. about 96° , which is being examined further. The expected isomeric form of xylose tetracetate has also been crystallized, found to melt at 59° and to have the specific rotation to the right of $+88$ in chloroform. This work will be published in detail later.—C. S. Hudson.

² Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

³ *Rec. trav. chim. Pays Bas*, 11, 106 (1892).

⁴ *Ber.*, 12, 1940 (1879).

⁵ *Ibid.*, 22, 1464 (1889).

⁶ *Ibid.*, 46, 4020 (1913).

to show a specific rotation of -25.3 in chloroform.¹ The substance is evidently the same as that which Fischer and Oetker have prepared, and the fact that it may be obtained from β -mannose at 0° by acetylation with acetic anhydride mixed with ZnCl_2 , as well as with pyridine as a catalyst, increases the probability that the substance is the beta form. Recently we have transformed this pentacetate into the isomeric alpha form by heating it in acetic anhydride solution with a small amount of ZnCl_2 . Although the spontaneous crystallization of the new pentacetate was very difficult to accomplish, an examination of the solubilities of the first crystals which were obtained suggested a method of operation by which the substance may be prepared with ease as beautiful crystals.

Preparation of the β -Pentacetate of Mannose by the Action of Acetic Anhydride and ZnCl_2 .²—Four grams of fused zinc chloride were dissolved in 40 g. of acetic anhydride, the solution was cooled to zero and 10 g. of very pure β -mannose were added a little at a time, the mixture being kept at zero with occasional shaking until all the sugar went into solution, which required about twenty-four hours. Ice water was then added and after a time the insoluble viscous phase crystallized. On recrystallization from 95% alcohol, β -mannose pentacetate was obtained in a yield of 45–50% of the theoretical. The substance was successively recrystallized from 95% alcohol until the specific rotation became constant. A solution consisting of 2.1073 g. pentacetate made up to 25 cc. with chloroform (*chloroformum purificatum*, U. S. P.) gave a negative rotation, -4.26 circular degrees, in a 200 mm. tube, hence $[\alpha]_D^{20} = -25.3^\circ$. A similar solution containing 4.534 g. pentacetate gave a specific rotation of -25.1° . The melting point of the substance was $117-8^\circ$ corr. These values agree with those found by Fischer and Oetker. An acetyl estimation, which was made by boiling in a quartz flask with reflux condenser half a gram of the pentacetate with 100 cc. of 0.25 *N* sulfuric acid during three hours, indicated 76.78% acetic acid, and in duplicate 77.22%, against 76.93% as the theoretical value for a mannose pentacetate.

Transformation of β -Mannose Pentacetate to the New Isomeric Alpha Form.—When the β -pentacetate was dissolved in acetic anhydride containing a small amount of ZnCl_2 , the rotation was found to change towards the right very slowly at room temperature but rapidly on the steam bath. After a constant value was reached, the solution was poured into cold water and the oily substance which separated was then thoroughly washed with cold water. The material was found to be soluble in hot water and such a solution on cooling and long standing slowly deposited crystals which proved to be the isomeric α -pentacetate. Further experiments have

¹ Unpublished communication.

² The directions for this preparation are based upon hitherto unpublished work by Mr. H. L. Sawyer and myself.—C. S. Hudson.

shown the following to be a more convenient method for the preparation of the substance. Twenty grams of β -pentacetate are dissolved in 30 cc. of acetic anhydride containing about 1 g. of fused zinc chloride and the solution is heated on the steam bath until no further change in the rotation is noticed, which requires about thirty minutes. The solution is cooled, mixed with 500 cc. of ice water, and the acid is neutralized with sodium bicarbonate. A thick, gummy substance separates and is removed, washed in cold water, and dissolved in boiling water. On cooling, the solution slowly deposits about 7 g. of crystals of the α -pentacetate in nearly pure condition. The substance has been recrystallized from water until the specific rotation became constant. The melting point of the pure material, dried in a vacuum desiccator over CaCl_2 and KOH , is 64° corr.

0.2246 and 0.3149 g. subs. yielded 0.4044 and 0.5681 g. CO_2 and 0.1164 and 0.1623 g. H_2O , in duplicate corresponding to 49.10 and 49.20% C and 5.79 and 5.77% H, respectively. Calc. for a mannose pentacetate 49.21% C and 5.68% H.

Acetyl determinations, made by boiling in a quartz flask with a reflux condenser 0.5 g. substance with 100 cc. 0.25 H_2SO_4 during three hours gave 77.11 and 77.18% acetic acid, which agree with the theoretical value for a mannose pentacetate, 76.93%.

In chloroform (*chloroformum purificatum* U. S. P.) solution 0.9197 g. of the α -pentacetate per 25 cc. of the solution gave a reading to the right, $+4.04$ circular degrees, in a 2 dcm. tube with sodium light, or $[\alpha]_D^{20} = +54.9^\circ$. A duplicate measurement, in which 1.2007 g. pentacetate were used, gave $[\alpha]_D^{20} = +55.1^\circ$.

Comparison of the Rotatory Powers of the Alpha and Beta Forms of Mannose Pentacetate with those of the Glucose Pentacetates.—If the molecular rotations of the α - and β -pentacetates of glucose are written $(+A + B)$ and $(-A + B)$, respectively, those of the corresponding mannose pentacetates may be considered, as a first approximation, to be $(+A + B')$ and $(-A + B')$, where B and B' have different values. It follows that the difference of the rotations of the mannose pentacetate pair is $2A$, which is equal to the difference for the glucose pentacetates. We have previously¹ found the molecular rotations of the glucose pentacetates in chloroform solution to be $+39,600$ for the alpha form and $+1,500$ for the beta, hence the difference is $38,100$. The difference in the specific rotations of the mannose pentacetates in the same solvent is $(55.0 + 25.2) = 80.2^\circ$, which corresponds to a molecular rotation difference of $+31,300$, since the molecular weight of the pentacetate is 390. There is thus some lack of agreement between these values, corresponding to 17° in specific rotation, which suggests that the change from the glucose chain, of rotation B , to the mannose chain, of rotation B' , may somewhat change the value of A . On the other hand, the agreement with theory appears sufficient to justify the nomenclature which has been adopted for the two pentacetates of mannose.

WASHINGTON, D. C.

¹ THIS JOURNAL, 37, 1264 (1915).

CRYSTALLINE *d*-FRUCTOSE PENTACETATEBy C. S. HUDSON AND D. H. BRAUNS.¹

Received March 12, 1915.

Progress in the investigation of fructose has always been impeded by the difficulty of crystallizing its derivatives. According to the accepted view of the constitution of fructose, its molecule contains five hydroxyl groups and therefore a pentacetate or two isomeric pentacetates, in case alpha and beta forms of fructose are postulated, should exist. Winter² acetylated fructose according to the Liebermann method with acetic anhydride and anhydrous sodium acetate, but did not obtain a crystalline product. Erwig and Koenigs³ also prepared an amorphous resin by the action of acetic anhydride and zinc chloride on fructose. They obtained analytical data which agree with the formula of a pentacetyl fructose, but since the substance was amorphous, its chemical individuality is doubtful. It would appear probable from the method of preparation that it was a mixture of isomeric pentacetates of fructose. Panormov⁴ prepared from fructose by a modification of Baumann's method of benzylation an amorphous product which had the composition of a penta-benzoylfructose, but its failure to crystallize prevented in this case also the establishment of convincing direct proof that five hydroxyl groups are present in fructose. Several years ago, one of us⁵ prepared a crystalline tetracetate of fructose, but the expected pentacetate was not obtained. Recently we have succeeded in preparing a pentacetate of *d*-fructose which crystallizes very readily, as is the case with fructose tetracetate.

Forty grams of very pure recrystallized *d*-fructose are added in the form of fine powder to a mixture of 240 cc. acetic anhydride and 10 cc. concentrated sulfuric acid, which is cooled by an ice and salt bath and vigorously stirred by a motor driven glass paddle. When the fructose is dissolved, which requires about an hour, the mixture is shaken with about 500 cc. of ice water, neutralized in a large dish with sodium bicarbonate, separated from the excess of solid bicarbonate by filtration, and the residue on the filter is washed with chloroform to dissolve the adhering acetylated sugar. The filtrate is extracted with chloroform for the same purpose. The chloroform solutions are mixed, dried with calcium chloride and distilled *in vacuo* to a small volume, 30-50 cc. This solution is then spread in a thin layer on a flat crystallizing dish and a strong current of air is passed over the yellowish fluid until the odor of chloroform disappears, and that of acetic anhydride becomes noticeable.

¹ Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

² *Ann.*, 244, 295 (1888).

³ *Ber.*, 23, 672 (1890).

⁴ *J. Russ. Phys. Chem. Soc.*, 1, 375 (1891).

⁵ Brauns, *Verslag v. d. Koninkl. Akad. v. Wetensch.*, Amsterdam, 1908, 577.

The sirup is then placed in a vacuum desiccator near potassium hydroxide and on stirring at intervals, it soon crystallizes to a solid mass. This is stirred in a mortar with some ether and filtered by suction, yielding about 16 g., or 20% of the theoretical, of pure *d*-fructose pentacetate of correct melting point and specific rotation. The substance may be easily recrystallized from ether and by slow evaporation brilliant, clear crystals may be obtained, measuring about 1 cm. in length and several mm. in width.

Fructose pentacetate melts at 108–109°. It is colorless, odorless and has a bitter taste. It is slightly soluble in cold water, insoluble in petroleum ether and readily soluble in benzene, chloroform, ether and alcohol. In comparison with fructose tetracetate, its solubility in ether and in alcohol is greater.

0.2919 and 0.2302 g. gave 0.5267 and 0.4147 g. CO₂ and 0.1515 and 0.1195 g. H₂O, corresponding to 49.21 and 49.13% C and 5.81 and 5.81% H; calc. for C₈H₇O(C₂H₅O₂)₅: 49.21% C, and 5.68% H.

The quantitative saponification of fructose pentacetate requires care, because the liberated fructose is so readily attacked by acid or alkali. Erwig and Koenigs¹ found the sugar to be slightly attacked by three hours' boiling with 0.1 *N* sulfuric acid. We observed a similar action and after trying various modifications, discarded the method of acid hydrolysis. It was found, however, that fructose pentacetate may be saponified readily by shaking at 0° with 0.1 *N* sodium hydroxide, a reagent which does not produce from fructose, under the same conditions, detectable amounts of acid, according to control experiments.

By shaking 0.4000 g. powdered fructose pentacetate with 75 cc. 0.1 *N* sodium hydroxide during two hours at 0° and titrating with 0.1 *N* sulfuric acid and phenolphthalein, the amount of acetic acid produced was found to be 73.99%. In a similar experiment of 3½ hours' duration, the value 77.20% was found, and in a third, lasting 5 hours, the value was 76.87%. The theoretical quantity for a fructose pentacetate is 76.93%. Evidently the saponification is complete after 3½ hours. The solution was levorotatory after saponification, indicating the regeneration of fructose.

The molecular weight of the fructose pentacetate was determined by the lowering of the freezing point of benzene. In three experiments, 1.789, 1.928 and 3.359 g. fructose pentacetate per 100 g. benzene gave the respective depressions, 0.226°, 0.242° and 0.415°, from which the values 396, 398 and 404 are calculated for the molecular weight in comparison with the theoretical value 390.

Fructose pentacetate can be obtained from benzene solution with one molecule of benzene of crystallization. This substance melts at 90° and on standing in the air readily loses benzene, which was recognized by its odor. On drying at ordinary temperature during one week, the substance lost 14.1% in reaching constant weight. Further drying at 70° did not decrease its weight. The formula C₁₆H₂₂O₁₁·C₆H₆ corresponds to 16.6% benzene.

The specific rotation of the fructose pentacetate was measured in chloro-

¹ *Lec. cit.*

form and in benzene solution. 2.500 g. fructose pentacetate without recrystallization were made up to 50 cc. with chloroform (*chloroformum purificatum*, U. S. P.), and the solution polarized in a 2 dcm. tube at 20° with sodium light 12.04 circular degrees to the left, hence $[\alpha]_D^{20} = -120.4^\circ$. After one recrystallization from ether 2.500 g. fructose pentacetate made up in the same manner rotated 12.09 circular degrees to the left, hence $[\alpha]_D^{20} = -120.9^\circ$. After a second recrystallization from ether, the material still rotated -120.9° , which is taken as the specific rotation of the pure substance. 1.000 g. of pure fructose pentacetate made up to 50 cc. with benzene rotated, under the above mentioned conditions, 4.22 circular degrees to the left, hence $[\alpha]_D^{20} = -105.5$ for its solution in benzene.

WASHINGTON, D. C.

THE VOLATILE OILS OF THE GENUS SOLIDAGO.

By EMERSON R. MILLER and JEMISON MIMS MOSLEY.

Received March 8, 1915.

The genus *Solidago*, commonly known as Golden-rod, is one of the larger genera of the plant family Compositae. It is quite widely and favorably known for the beauty which the golden-yellow flowers lend to late summer and early autumn, but is more or less unpopular as an alleged cause of hay fever.

Although a very large genus, numbering about seventy-five species in the United States alone, it has been of comparatively little practical value and consequently has received little attention at the hands of the phytochemist.

Of the four or five species which have been distilled, two, *Solidago canadensis* and *S. odora*, give a very fair yield of volatile oil and may, possibly, become of some economic importance. Only two of the oils thus far distilled, those of *Solidago canadensis*¹ and *S. nemoralis*² have received anything like a thorough chemical investigation.

The Volatile Oil of *Solidago rugosa*.

Solidago rugosa Mill. is an American species found in damp thickets and on the borders of fields from Newfoundland to Ontario and south-westward to the Gulf of Mexico. It grows from one to six feet high.

In 1893 Oberhauser³ made a chemical examination of the flowering plant and reported, among other things, a volatile oil present to the extent of 0.996%. The flowers and leaves were separately distilled with water. From the flowers he obtained a colorless oil having $d_{15} = 0.8486$; from the leaves a straw-colored oil having $d_{15} = 0.8502$. Both oils had an

¹ Report of Schimmel & Co., April, 1894, p. 57.

² THIS JOURNAL, 36, 2538 (1914).

³ Am. J. Pharm., 65, 122 (1893).

odor resembling origanum. Reactions with iodine and bromine indicated the presence of large amounts of terpenes. "On careful heating each began to boil at 130°."

From plants of this species collected near Auburn, Ala., we obtained by steam distillation of the fresh material a small amount of a light yellow oil, the yield being about 0.4%. The plants were in full bloom and were on the average three to four feet high. The material was carefully examined and was known to be free from other plants. Our determination of the plants was confirmed by comparison with specimens in the herbarium of the Alabama Polytechnic Institute.

The following physical and chemical properties were determined: d_{25}^{25} , 0.8620; α_D , -12.8°; n_D^{25} , 1.4813; saponification number, 4.22; saponification number after acetylation, 10.97. These values correspond to 1.47% of ester calculated as bornyl acetate and 1.67% of free alcohol calculated as borneol.

After saponification the oil was fractionated under diminished pressure, then under atmospheric pressure. The results are given in Table I.

TABLE I.

| No. of fraction, | Boiling temperature. | d_{25}^{25} . | α_D . (100 mm. tube.) | n_D^{25} . |
|------------------|----------------------|-----------------|---------------------------------|--------------|
| 1..... | Below 165° | 0.8520 | - 3.78° | 1.4688 |
| 2..... | 165-170° | 0.8560 | + 8.32° | 1.4700 |
| 3..... | 170-175° | 0.8530 | +24.04° | 1.4725 |
| 4..... | 175-180° | 0.8510 | | 1.4745 |
| 5..... | 180 | 0.9200 | | 1.4764 |
| 6..... | Residue | | | |

From Fraction 1, which formed the greater part of the oil, there was prepared a nitrosyl chloride, m. p. 103°. As will be seen the boiling temperature, specific gravity, and index of refraction of this portion of the oil all agree closely with those of α -pinene and there can scarcely be any doubt that the oil is composed mainly of that terpene. For similar reasons it may be said that Fraction 4 is most probably composed mainly of limonene. The higher specific gravity of the two intervening fractions shows conclusively that a third compound, probably β -pinene, is present. Fraction 5 contained the alcohol resulting from saponification. That a saponification number of 10.97 was obtained after acetylation is, however, not absolute proof that a free alcohol was present, since it has been shown by Bouchardat and Lafont¹ and by Sievers² that unsaturated hydrocarbons may be acetylated.

The Volatile Oil of *Solidago Odora*.

Solidago odora Ait., commonly known as Sweet Scented Golden-rod or Blue Mountain Tea, is a native of the United States, growing in dry

¹ *Compt. rend.*, 102, 171 (1886).

² University of Wisconsin, Science Series, *Bull.* 434 (1911).

or sandy soil on the borders of thickets and in open woods from New Hampshire to Florida, westward to Missouri and Texas. The stem is $1\frac{1}{2}$ to $3\frac{1}{2}$ feet high. The whole plant is strongly aromatic, having a pleasant odor resembling that of anise and a sweetish aromatic taste.

The leaves and flowering tops of this plant were official in the United States Pharmacopoeia from 1820 to 1870, being placed in the secondary list of the *Materia Medica*. At times it has occupied a rather important place among medicinal plants, having been used to cover the taste and odor of disagreeable medicines, also as a stimulant, carminative and stomachic. It has been much used as a domestic remedy to produce diaphoresis, allay colic and promote menstruation.

Golden-rod oil has been an article of commerce, in a small way, for many years, although it has probably been nothing more than a nondescript oil distilled from a mixture of weeds without any attempt at selection. "While a little true, scented golden-rod oil has probably been distilled here and there in an experimental way, we have never seen more than a few ounces at a time purporting to be such."¹

In 1891 Schimmel & Co.² obtained from *Solidago odora* by steam distillation a sample of oil which they described as strongly aromatic but not especially pleasant; density, 0.963.

In 1906 the same firm³ obtained from the United States two volatile oils, one of which they considered to be oil of *Solidago odora* and was described as follows: light yellow color, pleasant refreshing aroma; d_{15}° , 0.8904; α_D , -15° $14'$; ester number 34.2, after acetylation 59.9; did not dissolve to a clear solution in 10 volumes of 90% alcohol. By using 95% alcohol the solution was clear at first only. Turbidity was produced by addition of more than 1.5 volumes of 95% alcohol. Judging from the odor of the oil they considered the ester content to be composed mainly of bornyl acetate, the ester number found corresponding to about 12% of that ester.

Making all due allowance for variations known to occur in oils from the same source, the marked differences between the physical and chemical constants of the oil described by Schimmel & Co. and the oil distilled by us make it evident that the two were not obtained from plants of the same species.

The oil used in our investigation was obtained by steam distillation from fresh material consisting of the greater part of the flowering plant carefully examined and known to be free from other plants. The plant is easily distinguished from the other species of this genus by its linear-lanceolate, entire, shining leaves and their anise-like odor.

¹ Private communication from Dodge & Olcott Co.

² *Report*, Oct., 1891, p. 40.

³ *Ibid.*, April, 1906, p. 64.

TABLE II.

| No. of sample. | When distilled. | Yield. %. | Rotation 100 mm. tube. | No. of sample. | When distilled. | Yield. %. | Rotation 100 mm. tube. |
|----------------|-----------------|-----------|------------------------|----------------|-----------------|-----------|------------------------|
| 1..... | Sept. 20 | 0.64 | +10.75° | 6..... | Sept. 30 | 1.32 | +11.75° |
| 2..... | Sept. 21 | 1.14 | +10.75° | 7..... | Oct. 1 | 1.14 | +12.02° |
| 3..... | Sept. 21 | 1.09 | +15.75° | 8..... | Oct. 2 | 1.13 | +20.12° |
| 4..... | Sept. 25 | 1.18 | +11.80° | 9..... | Oct. 4 | 1.19 | +16.75° |
| 5..... | Sept. 27 | 1.53 | +13.80° | 10..... | Sept. 12 | 0.65 | + 9.33° |

The results obtained on this oil are given in Table II. By reference to the table it is seen that the yield was above 1% in every case but two. Botanists describe a variety of *Solidago odora* characterized by having odorless leaves. We found a few plants of this kind, but it seems hardly probable that they were present in sufficient quantity to account for this low yield.

In the case of Sample 5, where the yield was unusually high, the material was collected mainly in open fields which had been cultivated. These plants were decidedly more branched and consequently possessed a much larger quantity of leaves and flowers in proportion to stem. As there is very little oil in the stem this would, of course, give a larger percentage of oil. Sample 10 was obtained from plants which had been transplanted and cultivated in an open field. The plants were harvested about the 12th of September and after drying were shipped to Madison, Wisconsin, where they were distilled about three months later. The yield would undoubtedly have been considerably higher if the plants had been collected two weeks later and distilled in the fresh condition.

The greater part of the oil used in this investigation consisted of the first nine samples which were mixed after the optical rotation of each had been determined. The color of the oil was slightly yellowish, the odor somewhat like that of anise and at the same time somewhat suggestive of safrol. The taste was warm and sweetish, very noticeably less sweet than oil of anise. The following constants were determined: d_{25}^{25} , 0.9310°; α_D , +13.72°; n_{D28} , 1.5065; saponification number, 7.9; acid number, 0.63; % of OCH_3 , 15.9. These saponification values correspond to 3.11% of ester calculated as bornyl acetate and 2.96% of free alcohol calculated as borneol. Considering the methoxy compound to be methyl chavicol, this value for OCH_3 would indicate that 75.89% of the oil consists of methyl chavicol.

For Sample 10, the oil from cultivated plants, the following constants were found: d_{15}^{25} , 0.9450°; α_D , +9.33°; n_{D24} , 1.5140; saponification number, 8.9; after acetylation, 19.4. One cc. of the oil with two drops of 90% alcohol gave a turbid mixture. One volume of the oil with 0.4 volume of 90% alcohol produced a clear mixture. One volume of the oil gave a turbid mixture after the addition of 15 volumes of the alcohol.

Action of Reagents on the Oil.—With a drop of conc. nitric acid the oil

gives a bright green color which soon changes to reddish brown. With an excess of acid a bright red color is produced. With conc. sulfuric acid a brownish purple soon becoming rose colored on the edges is produced. Conc. hydrochloric acid causes a dull red color. Glacial acetic acid dissolves it without change of color. Conc. formic acid causes a purplish color which soon changes to reddish brown. Conc. aqueous solution of potassium hydroxide produces no visible change, but when boiled with 0.5 *N* alcoholic potassium hydroxide the oil becomes very dark colored.

Test for Phenol.—5 cc. of the oil were shaken in a cassia flask with an excess of 5% aqueous solution of potassium hydroxide and the oil then brought into the graduated neck of the flask. No diminution in the volume of the oil was observed, showing the absence of phenols, or the presence of not more than traces.

Test for Aldehydes and Ketones.—With Schiff's reagent for aldehydes no color was produced within two minutes. With sodium bisulfite and hydroxylamine negative results were obtained, showing that aldehydes and ketones are either absent or present only in traces.

Test for Anethol.—Since the odor of the oil suggested the possible presence of anethol, some of the oil was kept in a freezing mixture of ice and salt for several hours, the sides of the container being repeatedly rubbed with a glass rod. No solid separated. Information obtained by fractionation of the oil also showed that anethol is either absent or present in very small amount.

Test for Methoxy Compounds. Quantitative Determination of the Methoxy Group.—The only substance known to have an odor similar to that of anethol is its isomer methyl chavicol. If this substance were the bearer of the characteristic odor the oil should give a positive result when treated according to the method of Zeisel.¹ In order to throw light on this question an estimation was made, following Perkin's² modification of the Zeisel method. The amount of silver iodide obtained corresponded to 15.9% of methoxyl. To determine whether the alkoxyl present was methoxyl or ethoxyl or possibly both, the alkyl halide formed by the action of boiling hydriodic acid on the oil was conducted into an alcoholic solution of dimethyl aniline. A beautiful, white, crystalline substance was obtained having the melting point 212–213°. The melting point given for trimethyl phenyl ammonium iodide is 212–214°, and for dimethyl ethyl phenyl ammonium iodide is 124°. Consequently the alkoxyl group in the oil must be the methoxyl group.

Saponification and Fractionation of the Oil.—The oil was heated one hour on a boiling water bath with an excess of potassium hydroxide

¹ *Monatsh.*, 6, 989 (1885).

² *J. Chem. Soc.*, 83, 1367 (1903).

in alcoholic solution, and the greater part of the alcohol removed by distillation. The liquid remaining in the distilling flask was mixed with a large volume of water, the oil which separated was removed, washed till neutral, dried with anhydrous sodium sulfate and fractionated under a pressure of 20 mm. The five fractions thus obtained were refractionated three times under atmospheric pressure. The results are given in Table III.

TABLE III.

| No. of fraction. | Boiling temperature. | d_{25}^{25} . | n_D . | $n_{D18.9}$. |
|------------------|----------------------|-----------------|---------|---------------|
| 1..... | 165-180° | 0.8440 | +68.56 | |
| 2..... | 180-210° | 0.8930 | +48.34 | |
| 3..... | 210-212° | 0.9640 | + 0.25 | 1.5240 |
| 4..... | 212-225° | 0.9680 | + 0.20 | |
| 5..... | 225-240° | | | |

The constants given for Fraction 3 are for that fraction after it was again repeatedly redistilled. From fraction 225-240° there was obtained a fraction boiling at 236-240°. $n_{D18.9}$ for this fraction was 1.5295.

Test for Pinene.—From Fraction No. 1 a nitrosyl chloride, m. p. 103° was prepared by the method of Wallach¹ and also by the method of Ehestaedt.² From this compound both a nitrol-piperidide and a nitrol-benzylamine were prepared, but their behavior in regard to melting point was such as to make the presence of pinene doubtful.

From the alcohol distilled from the saponification mixture there was obtained, by dilution with water, a small amount of a hydrocarbon having the odor of pinene. From it also a nitrosyl chloride was prepared having the m. p. 103°.

Test for Phellandrene.—Fractions Nos. 1 and 2 were tested for phellandrene by the method of Wallach and Gildemeister³ for preparing phellandrene nitrosite but with negative results in both cases.

Identification of Methyl Chavicol.—The odor of the oil is generally described as being anise like, but the odor of Fraction No. 3 suggests both anethol and safrol. Indeed, the odor of safrol is so pronounced that several persons familiar with volatile oils mistook this fraction for oil of sassafras.

Although the odor of this fraction may be considered as somewhat anise-like the absence of anethol is shown in several ways, as follows: (1) Its taste is only moderately sweet while that of anethol is decidedly sweet; (2) its boiling point is too low by 10-12°; (3) when subjected to a freezing mixture it could not be made to solidify or deposit any crystals, whereas anethol is readily crystallized when subjected to cold. On the

¹ *Ann.*, 245, 251 (1888).

² *Report of Schimmel & Co.*, April, 1910, p. 104.

³ *Ann.*, 246, 282 (1888).

other hand its odor, taste, boiling point, density, index of refraction and its being almost optically inactive all agree in suggesting methyl chavicol.

Preparation of Anisic Acid.¹—In order to obtain further knowledge of the chemical nature of this fraction, 25 g. were shaken with three liters of a warm 3% solution of potassium permanganate, the MnO_2 filtered off, the filtrate evaporated to a small volume and acidified with dilute sulfuric acid. A white solid separated, which, after recrystallization from alcohol, was obtained in brilliant needles having the melting point 184° . The melting point of anisic acid is given as 184.2° . A methoxyl estimation of the compound obtained in this experiment gave 19.95% of methoxyl; calculated for $C_6H_4 \begin{cases} OCH_3 (1) \\ COOH (4) \end{cases}$, $OCH_3 = 20.39\%$. The com-

pound resulting from the oxidation of this fraction of the oil is, therefore, anisic acid and the experiment proves that that part of the oil which boils at $210-212^\circ$ consists mainly of anethol or of methyl chavicol.

Preparation of Homoanisic Acid.¹—30 g. of this fraction were shaken in the cold with 20 g. each of potassium permanganate and acetic acid in two liters of water. On completion of the reaction the liquid was made alkaline by the addition of sodium carbonate, filtered, the filtrate evaporated to a small volume, acidified with dilute sulfuric acid and extracted with ether. On evaporation of the ether there was obtained a white solid. When crystallized from hot water it was obtained in beautiful, shining plates having the melting point $85-86^\circ$. The melting point of homoanisic acid is given at 86° .

Since methyl chavicol on oxidation yields homoanisic acid and anethol does not, this experiment proves that the methoxy compound contained in this fraction of the oil is methyl chavicol.

Further Examination of the Fraction Boiling at $210-212^\circ$.—That this fraction is not composed wholly of methyl chavicol was shown in several ways. An estimation of methoxyl gave 16.98% (OCH_3); calculated for methyl chavicol, $C_6H_4 \begin{cases} CH_2-CH=CH_2 (1) \\ OCH_3 (4) \end{cases}$, (OCH_3) = 20.94%. Al-

though the original oil was saponified before it was fractionated this fraction showed an ester number of 9.12, corresponding to 3.19% of ester calculated as bornyl acetate and 2.51% of combined alcohol calculated as borneol. After acetylation an ester number of 46.85 was obtained, corresponding to 13.35% of total alcohol and 10.84% of free alcohol, calculated as borneol.

Test for Camphor.—The fractions boiling at $195-210^\circ$ and $210-212^\circ$ were separately examined for camphor by the usual method of preparing

¹ Bertram and Walbaum, *Arch. Pharm.*, 235, 179, 182 (1897).

camphor oxime, but from neither fraction could any camphor oxime be separated. The experiment was repeated with both fractions but the results were also negative. This shows, therefore, that practically no camphor exists in the oil.

Identification of Borneol.—Although Schimmel & Co. expressed the view that bornyl acetate was a constituent of an American golden-rod oil which they considered to be oil of *Solidago odora*, there is nothing whatever in the odor of the genuine oil that suggests either bornyl acetate or free borneol. In fact, the amount of methyl chavicol present is so large that the odor of a considerable quantity of either the acetate or the free alcohol would be completely masked. However, since acetylation indicated the presence of a considerable amount of free alcohol in this fraction and since the boiling point is practically that of borneol, the fraction boiling at $210-212^{\circ}$ was treated as follows: 35 cc. were shaken one hour with 20 g. of potassium dichromate and 25 g. of conc. sulfuric acid in 200 cc. of water. The mixture was then made slightly alkaline with sodium carbonate and distilled with steam. 31 cc. of oil were recovered. This was boiled one hour on a water bath with 20 g. of hydroxylamine hydrochloride and 30 g. of sodium hydroxide in 250 cc. of alcohol. The mixture was then diluted with water, the oil which separated was removed and the alkaline liquid shaken out with ether. The mixture was then acidified slightly with acetic acid and again shaken out with ether. On evaporation of the ether there was obtained a thick, syrupy, brown mass, from which a small amount of a crystallized substance separated on standing. This was obtained almost colorless by pressing between porous plates. An attempt was made to recrystallize it from dilute alcohol, but, unlike camphor oxime, it was quite readily soluble. From its solution in diluted alcohol it was recovered by extraction with ether. On evaporation of the ether a syrupy liquid remained, which on standing a short time solidified to a white, crystalline mass. After drying between filter paper and then in a desiccator it melted at 45° .

Since borneol could not be identified in this way, recourse was had to the method of Haller¹ for the separation of borneol and camphor by conversion of the former into acid bornyl succinate, using, however, phthalic anhydride instead of succinic acid. 100 cc. of the fraction were heated with 15 g. of phthalic anhydride in a flask in a glycerin bath at $150-160^{\circ}$ for about fifty hours. On cooling, the oil was poured off from the phthalic anhydride which had crystallized out, then dissolved in ether and the ethereal solution shaken several times with a 5% solution of sodium carbonate. This solution was treated with sodium hydroxide and then distilled. A small amount of a white solid collected in the condensing tube. This product was crystallized from petroleum ether, sublimed

¹ *Compt. rend.*, 108, 1308 (1889).

and again crystallized from petroleum ether. It was obtained in hexagonal plates, melting point $203-204^{\circ}$. From this compound a phenyl urethane was prepared having the melting point $138-139^{\circ}$. This experiment proves that borneol is a constituent of the oil.

The bornyl phenyl urethane was crystallized from hot petroleum ether, but before it separated a few larger crystals were formed which melted at $149-150^{\circ}$. The formation of this compound seems to indicate the presence of a second alcohol in the oil.

Fractionation of the Oil from Cultivated Plants.—Sample No. 10.—After saponification this sample was fractionated under ordinary pressure. In Table IV physical constants are given for these fractions.

TABLE IV.

| No. of fraction. | Boiling temperature. | $n_{D20.5}^{\circ}$. | α_D . | $d_{25}^{25^{\circ}}$. |
|------------------|----------------------|-----------------------|-----------------|-------------------------|
| 1..... | $170-176^{\circ}$ | 1.4735 | $+62.6^{\circ}$ | 0.8408 |
| 2..... | $176-180^{\circ}$ | 1.4769 | $+71.0^{\circ}$ | |
| 3..... | $180-195^{\circ}$ | 1.4880 | $+57.4^{\circ}$ | |
| 4..... | $195-210^{\circ}$ | 1.5118 | $+15.4^{\circ}$ | |
| 5..... | $210-212^{\circ}$ | 1.5210 | $+0.7^{\circ}$ | |
| 6..... | $212-222^{\circ}$ | 1.5221 | $+0.1^{\circ}$ | |
| 7..... | $222-236^{\circ}$ | 1.5260 | -0.2° | 0.9840 |
| 8..... | Residue | 1.5505 | | |

A nitrosyl chloride was prepared from Fraction 1 by the method of Wallach.¹ After filtering out the crystals which first separated two further quantities of the nitrosyl chloride were obtained in succession by the addition of alcohol to the filtrate. The melting points, in order, of these products were 103° , $101-102^{\circ}$, $99-101^{\circ}$. A nitrol-piperidide was apparently formed but not in sufficient quantity to permit of purification and melting-point determination.

Fractions 2 to 7 inclusive were treated with concentrated formic acid. A pronounced purplish color was produced with Fraction 2. A similar color was formed with the next four fractions, but with gradually diminished intensity. With Fraction 7 no color was produced. These tests are of some importance as they show that the substance which produces the characteristic purplish color when the oil is treated with conc. formic acid is found among the lowest boiling constituents of the oil, but whether it is a terpene or not remains to be proved. We are not aware that this reaction has been reported for any terpene. With conc. nitric acid Fraction 4 gave a green color.

Although the data obtained are not sufficient to establish the identity of a low boiling compound, the physical constants of Fraction 1 may be considered proof of the presence of at least one terpene. It will also be seen that these constants are in better agreement with those of sabinene

¹ *Ann.*, 245, 251 (1888); 253, 251 (1889).

or sylvestrene than with those of α -pinene. The optical rotation of Fraction 2 shows that at least two compounds are present which have a lower boiling point than that of methyl chavicol. While the physical constants given for Fraction 2 may be considered as an indication of the presence of limonene, mixed with one or more other terpenes of lower optical rotation, there was nothing in the odor to suggest this.

Examination for Acids. Volatile Acids.—The aqueous alkaline liquid resulting from the saponification of the oil was concentrated on the water bath, filtered and acidified with dil. H_2SO_4 and then steam distilled. The distillation was continued until the distillate was only faintly acid. The distillate was collected in four fractions. Each fraction was made slightly alkaline with sodium hydroxide and concentrated on a water bath. Although there was an excess of alkali there was decomposition and loss of acid as indicated by the odor. The solutions were then treated with silver nitrate solution, drop by drop, until the sodium hydroxide was removed. The remaining precipitate was collected, dried and ignited. The percentage of metallic silver obtained was as follows: Fraction 1, 33.67%; Fraction 2, 39.8%; Fraction 3, 69.45%; Fraction 4, 73.9%. The silver salts were all quite dark in color. Whether the reduction was due to the presence of formic acid could not be satisfactorily established. From the data obtained it can not be stated what acids are present though there must be at least three volatile acids present.

Nonvolatile Acids.—The residue remaining in the flask after steam distillation was heated with barium carbonate and water, filtered and the filtrate treated with silver nitrate solution. A light yellowish precipitate was obtained, which, after drying and ignition, yielded 25.22% metallic silver.

Summary.

The oil of *Solidago rugosa* is composed mainly of terpenes, of which, at least, three are present. That α -pinene is one of these is highly probable. In addition there also appears to be present at least one ester and one free alcohol, 1.47% of ester calculated as bornyl acetate and 1.67% of alcohol calculated as borneol.

The oil of *Solidago odora* contains the following:

1. Terpenes, 10–15%.
2. Esters, about 3%, calculated as bornyl acetate.
3. Borneol and possibly another alcohol, the total percentage of free alcohol being about 3% calculated as borneol.
4. Methyl chavicol, forming about 75% of the oil.
5. A small amount of volatile fatty acids, at least three.
6. A small amount of nonvolatile acid.

[CONTRIBUTION FROM THE LABORATORY OF AGRICULTURAL CHEMISTRY OF THE UNIVERSITY OF NEBRASKA EXPERIMENT STATION.]

ON THE COLLOIDAL SWELLING OF WHEAT GLUTEN.¹

BY FRED W. UPSON AND J. W. CALVIN.

Received March 1, 1915.

The colloidal swelling of wheat gluten is of interest in connection with the general problem of water absorption by animal and plant tissues as elaborately investigated by Fischer² and his coworkers, and in connection with the theory and practice of bread making. Wood³ and Wood and Hardy⁴ have shown that wheat gluten is an emulsoid colloid and that when in contact with a solution its properties depend upon the concentration of acid and salts in that solution.

Wood's experiments were carried out by immersing small bits of gluten suspended over glass rods in beakers containing solutions of varying concentration of different acids, both with and without the presence of salts, and noting the effect of the different solutions on "disintegration" and "loss of cohesiveness" of the gluten. As these changes in the properties of the gluten are best regarded in our more modern terms of colloid chemistry as expressions of a change in the degree of dispersion of the colloid, and as these changes while often associated with, have in reality nothing to do with the changes in the *hydration capacity* of the colloid, it seemed to us that our experiments dealing with this second problem were worthy of record, especially since the way in which they were carried out was an entirely different one from that adopted by Wood and Hardy. The experiments are also of interest in that they substantiate the important work of Fischer and others on the general problem of water absorption by proteins.

The colloidal swelling of animal proteins was first studied by F. Hofmeister.⁵ It has since been extensively worked upon by Pauli,⁶ Spiro,⁷ Ostwald,⁸ Fischer² and others. Gelatin swells more in the solution of any acid than it does in pure water. The amount of swelling in a given time for a given acid varies directly with the concentration of the acid

¹ This paper was originally accepted for publication in THIS JOURNAL for July, 1914. The papers by Wood and by Wood and Hardy came to our notice after we had returned our proof. We withdrew our paper and now present it with the revisions made necessary because of the previous work of these two authors. The experimental details of our work were sent Dr. Fischer early in May, 1914, and are quoted by him in his "Oedema and Nephritis," second edition, New York, 1915, recently issued.

² Fischer, *Oedema and Nephritis*, Sec. Ed., N. Y. (1915).

³ Wood, *J. Agr. Sci.*, **2**, 267 (1907).

⁴ Wood and Hardy, *Proc. Roy. Soc. London*, (B) **81**, 38 (1909).

⁵ Hofmeister, *Arch. Exp. Path. u. Pharm.*, **27**, 395 (1890).

⁶ Pauli, *Pflüger's Arch.*, **67**, 219 (1897); **71**, 1 (1898).

⁷ Spiro, *Beit. Chem. Physiol.*, **5**, 276 (1904).

⁸ Ostwald, *Pflüger's Arch.*, **108**, 577 (1905).

up to a certain point. Thus Ostwald found that $N/38$ hydrochloric acid gave a maximum swelling of gelatin plates after twenty-four hours. With increasing concentrations of the acid beyond this point, the absorption of water became less.

While gelatin swells more in the solution of any acid than it does in pure water, the various acids do not bring about the same degree of swelling when equinormal solutions are compared. Ostwald found the order in which the different acids cause gelatin to swell to be: hydrochloric, nitric, acetic, sulfuric, boric.

The addition of any salt to the solution of an acid decreases the amount that gelatin will swell in that solution. Fischer¹ has shown that, for a given acid, the effect of the salt in decreasing the amount of swelling of gelatin increases with increasing concentration of the salt. If the concentration of salt is made high enough the effect of the acid may be almost or entirely suppressed.

Equimolar solutions of different salts do not produce the same effect in diminishing water absorption by gelatin. Thus Fischer found when different sodium salts are compared that the chloride and nitrate show the least effect, the phosphate and tartrate the greatest, the acetate and sulfate an intermediate one. Again when different salts of the same cation with different anions were compared (as a series of chlorides), he found that the ions like those of the monovalent alkalis show the least retarding effect, those of the trivalent metals like iron and aluminium the greatest, while the bivalent ones of calcium and magnesium fall between.

A further fact is to be noted. Nonelectrolytes, like sugar, alcohol and urea produce a much less marked antagonistic effect on the absorption of water by gelatin in acid and neutral solution than do neutral salts.²

Fischer finds that what holds for gelatin as regards water absorption holds also for fibrin³ and indeed for animal colloids⁴ in general, such as frog muscle, sheep eyes, catgut and the like.

Experimental Part.

The gluten for the following experiments was prepared by washing the starch from flour under a stream of distilled water. We found the character of the gluten to be quite different when tap-water, which contains salts, was used in place of distilled water, being tougher and more elastic and smaller in bulk, just as pointed out by Wood and Hardy.⁵ Since we wished to avoid the effect of any salts which might be absorbed by the gluten from the tap-water, all samples of gluten were prepared

¹ *Loc. cit.*

² Fischer and Sykes, *Science*, 37, 486 (1913); *Koll. Z.*, 14, 215 (1914).

³ Fischer and Moore, *Am. J. Physiol.*, 20, 313 (1907); *Pflüger's Arch.*, 125, 99 (1908); *Koll. Z.*, 5, 197 (1909).

⁴ Fischer, *Pflüger's Arch.*, 124, 69 (1907).

⁵ Wood and Hardy, *Proc. Roy. Soc. London*, (B) 81, 38 (1909).

with distilled water. The gluten ball was pressed out between glass plates to a fairly uniform thickness. After standing some time between the plates (during which time some fluid was usually squeezed off), discs could be cut from the gluten with a large cork borer, which were fairly uniform as to surface and weight. The discs were weighed to the nearest centigram and placed in the solution for exactly two hours, when they were removed, drained on a Buchner funnel and weighed again. The method is necessarily somewhat crude because the gluten is moist when weighed originally and because of the variation in the amount of water which mechanically adheres to the discs. Nevertheless, when the average of a number of determinations is taken the results are surprisingly uniform.

TABLE I.—LACTIC ACID.

| Conc. of acid. | Wt. of water absorbed in g. per g. of moist gluten. | | | | Average. |
|-------------------|---|------|-------|-------|----------|
| | a. | b. | c. | d. | |
| None | 0.046 | ... | 0.075 | 0.043 | 0.055 |
| 0.002 <i>N</i> | 1.30 | 1.31 | 1.02 | 1.07 | 1.18 |
| 0.005 <i>N</i> | 1.42 | 1.54 | 1.35 | 1.55 | 1.46 |
| 0.01 <i>N</i> | 1.51 | 1.77 | 1.44 | 1.55 | 1.57 |
| 0.02 <i>N</i> | 1.60 | 1.55 | 1.53 | 1.61 | 1.57 |
| 0.04 <i>N</i> | 1.48 | 1.51 | 1.35 | 1.42 | 1.44 |
| 0.1 <i>N</i> | 1.37 | 1.38 | 1.07 | 1.28 | 1.27 |
| 0.2 <i>N</i> | 1.23 | 1.15 | 1.11 | 1.19 | 1.15 |
| 0.5 <i>N</i> | 1.01 | Lost | 0.99 | 1.08 | 1.03 |

TABLE II.—ACETIC ACID.

| Conc. of acid. | Wt. of water absorbed in g. per g. of moist gluten. | | | Average. |
|-------------------|---|------|-------|----------|
| | a. | b. | c. | |
| None | 0.03 | 0.01 | —0.03 | 0.01 |
| 0.002 <i>N</i> | 1.11 | 1.47 | 1.30 | 1.29 |
| 0.005 <i>N</i> | 1.39 | 1.58 | 1.90 | 1.62 |
| 0.01 <i>N</i> | 1.43 | 1.58 | 1.87 | 1.63 |
| 0.02 <i>N</i> | 1.56 | 1.76 | 1.96 | 1.76 |
| 0.04 <i>N</i> | 1.80 | 1.88 | 2.03 | 1.90 |
| 0.1 <i>N</i> | 1.62 | 2.06 | 1.86 | 1.85 |
| 0.2 <i>N</i> | 1.51 | 1.82 | 1.76 | 1.69 |
| 0.5 <i>N</i> | 1.49 | 1.69 | 1.66 | 1.61 |

TABLE III.—HYDROCHLORIC ACID.

| Conc. of acid. | Wt. of water absorbed in g. per g. of moist gluten. | | Average. |
|-------------------|---|-------|----------|
| | a. | b. | |
| None | 0.00 | 0.00 | 0.00 |
| 0.002 <i>N</i> | 1.47 | 1.28 | 1.37 |
| 0.005 <i>N</i> | 1.63 | 1.44 | 1.54 |
| 0.01 <i>N</i> | 1.67 | 1.37 | 1.52 |
| 0.02 <i>N</i> | 1.37 | 1.12 | 1.23 |
| 0.04 <i>N</i> | 0.83 | 0.68 | 0.75 |
| 0.1 <i>N</i> | 0.14 | 0.16 | 0.15 |
| 0.2 <i>N</i> | —0.097 | 0.01 | —0.04 |
| 0.5 <i>N</i> | —0.19 | —0.09 | —0.14 |

The curves showing the amount of water absorption with increasing concentration of acid for Tables I, II, and III are shown in Fig. 1. The curves represent the average for four, three and two determinations, respectively, for lactic, acetic, and hydrochloric acids. The concentrations of acid are plotted along the horizontal, and the water absorption in grams per gram of moist gluten is plotted on the vertical axis. An inspection of these curves brings out some interesting facts. For hydrochloric acid the maximum absorption is obtained with a concentration of 0.005 *N*, while the concentration for maximum absorption with lactic acid lies between 0.01 *N* and 0.02 *N* and for acetic acid is 0.04 *N*. It is to be noted that for concentrations above the one for maximum absorption, the curves do not fall off at anything like the same rate for the three acids. The curve for hydrochloric falls much more rapidly than the curves for the other two. This agrees with the results as found by Fischer¹ for fibrin and by Ostwald for gelatin.² Fischer obtained maximum swelling of both fibrin and gelatin in approximately 0.025 *N* hydrochloric acid and diminished swelling for concentration above this.

Of special interest is the fact that both lactic and acetic acids show concentrations of optimal swelling for gluten. Such an optimal swelling of a protein in a "weak" acid, has never before been observed. It does not occur in gelatin, fibrin and the other animal colloids thus far studied. The swelling of gluten also diminishes much more rapidly with increasing concentration of hydrochloric acid beyond the optimal point, than does the swelling of gelatin or fibrin. It is also of interest that moist gluten *loses* water in the higher concentrations of hydrochloric acid 0.2 *N* and 0.5 *N*. We have established that gluten discs lose weight in these higher concentrations of acid because of loss of water and not because of "solution" of the gluten. Examination of the surrounding fluids in these higher concentrations of acid fails to reveal more than traces of dissolved protein, whereas in the lower concentrations where greatest swelling takes place considerably more protein is dissolved. When gluten swells in dilute acid the discs puff up and take on an appearance somewhat resembling cotton balls, finally becoming transparent, soft and gelatinous. In 0.2 *N* and 0.5 *N* hydrochloric acid the discs do not change in appearance or in physical properties except to become tougher and more elastic just as in salt solutions. Discs which have lost water in 0.5 *N* hydrochloric acid gain water and become soft and gelatinous when placed in more dilute acid. Those which have absorbed water to more than double their weight in the more dilute acid, lose it if placed in 0.5 *N* acid. The taking up and giving off of water is, in other words, largely reversible.

When any salt is added to an acid in which a gluten disc is swelling,

¹ Fischer, *Oedema and Nephritis*, Sec. Ed., N. Y. (1915), pp. 44, 48.

² *Loc. cit.*

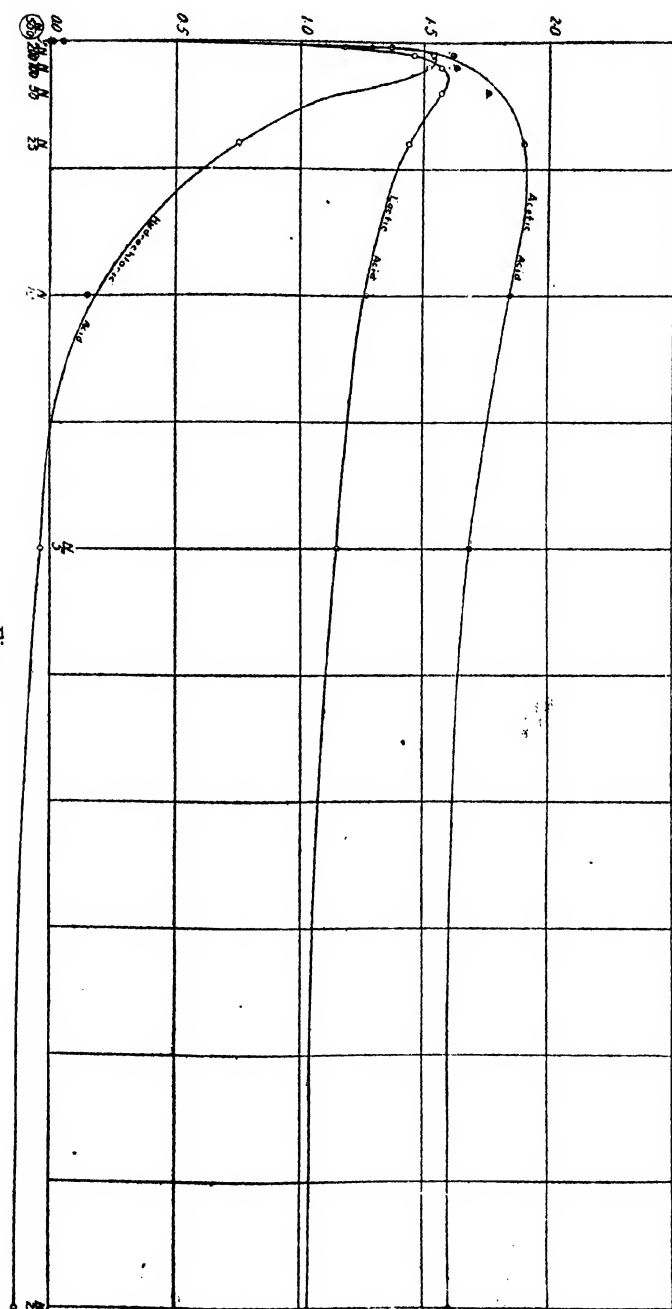


Fig. 1.

the swelling is much reduced. This is shown in Table IV and Fig. 2 which is based upon the results shown in this table.

TABLE IV.—0.005 *M* SALT SOLUTIONS AND VARYING CONCENTRATIONS OF LACTIC ACID.

| Conc. of acid solution. | Wt. of water absorbed in g. per g. of moist gluten. | | | | |
|-------------------------|---|-----------------------------|---------------------|---------------------------|----------|
| | 0.005 <i>M</i> $K_2C_4H_4O_6$. | 0.005 <i>M</i> K_2HPO_4 . | 0.005 <i>M</i> KCl. | 0.005 <i>M</i> $CaCl_2$. | No salt. |
| No acid | —0.11 | —0.14 | —0.11 | —0.11 | —0.01 |
| 0.002 <i>N</i> | —0.06 | —0.012 | 0.49 | 0.25 | 1.39 |
| 0.005 <i>N</i> | 0.04 | 0.16 | 0.77 | 0.42 | 1.50 |
| 0.01 <i>N</i> | 0.25 | 0.63 | 0.98 | 0.57 | 1.81 |
| 0.02 <i>N</i> | 0.55 | 0.86 | 1.28 | 0.68 | 1.87 |
| 0.04 <i>N</i> | 0.73 | 0.97 | 1.30 | 0.89 | 1.72 |
| 0.1 <i>N</i> | 1.06 | 1.12 | 1.43 | 0.96 | 1.69 |

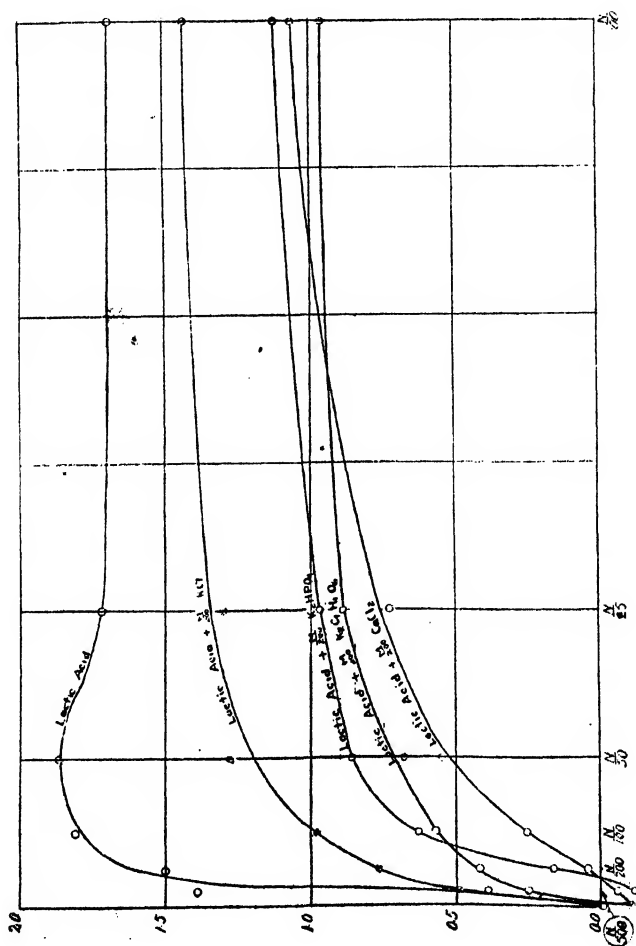
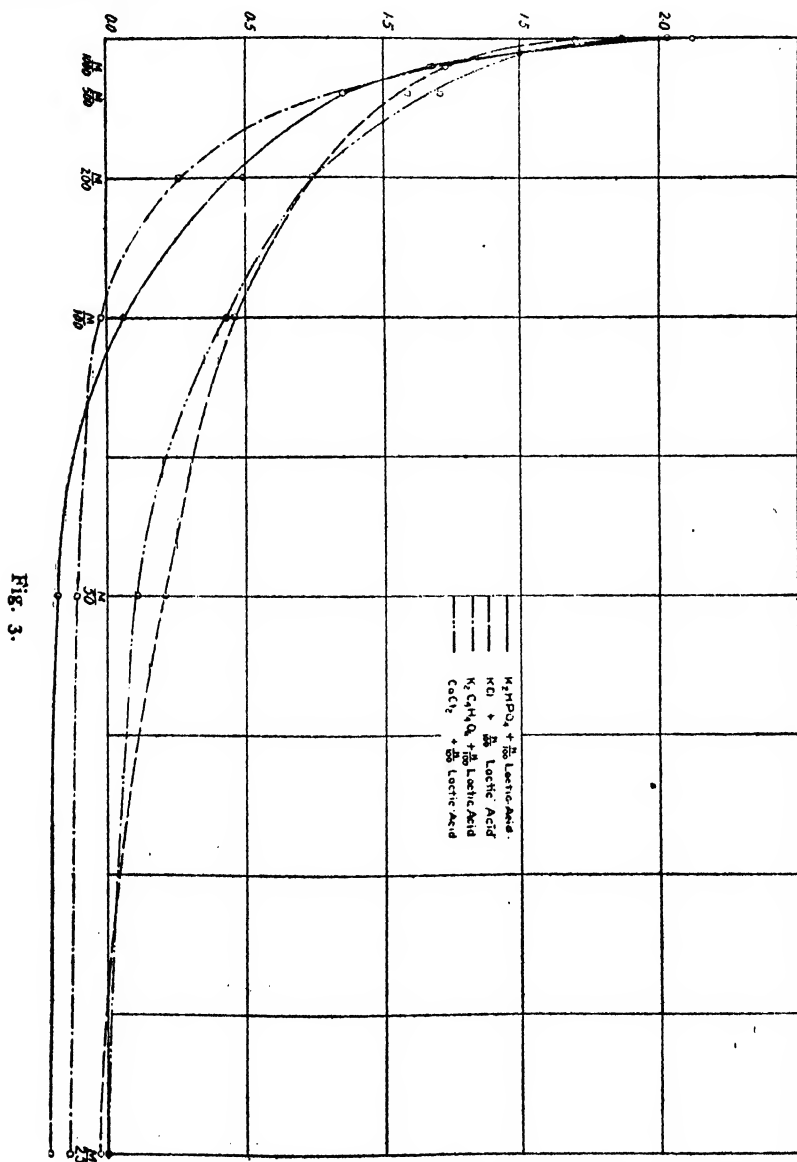


Fig.

In Table V are given the figures showing the effect of varying concentrations of four salts and also of glycocholl on the absorption of water by gluten in the presence of 0.01 *N* lactic acid. The results are shown graphically in Fig. 3.



In all cases there is a rapid decrease in water absorption with increase in the concentration of the salt. In the higher concentrations of phos-

phate and tartrate the gluten disc drops to a weight below that of the original moist disc.

TABLE V.—0.01 *N* LACTIC ACID AND VARYING CONCENTRATIONS OF SALTS AND OF GLYCOCOLL.

| Conc. of salt solution. | Wt. of water absorbed in g. per g. of moist gluten. 0.01 <i>N</i> lactic acid and | | | | |
|-------------------------|--|-----------------------------------|---|---------------------|-----------|
| | KCl. | K ₂ HPO ₄ . | K ₂ C ₄ H ₄ O ₆ . | CaCl ₂ . | Glycocol. |
| No salt | 1.70 | 2.12 | 1.87 | 2.02 | 1.70 |
| 0.0001 <i>M</i> | 1.23 | 1.17 | 1.18 | 1.50 | .. |
| 0.002 <i>M</i> | 1.09 | 0.85 | 0.85 | 1.21 | 1.57 |
| 0.005 <i>M</i> | 0.74 | 0.49 | 0.26 | 0.85 | 1.65 |
| 0.01 <i>M</i> | 0.46 | 0.06 | —0.02 | 0.43 | 1.29 |
| 0.02 <i>M</i> | 0.21 | —0.18 | —0.11 | 0.11 | 1.21 |
| 0.04 <i>M</i> | —0.03 | —0.21 | —0.14 | 0.00 | 1.14 |
| 0.1 <i>M</i> | .. | .. | .. | .. | 0.71 |
| 0.2 <i>M</i> | .. | .. | .. | .. | 0.53 |
| 0.4 <i>M</i> | .. | .. | .. | .. | 0.50 |

At the concentration of 0.02 *M* the order of salts as regards their effect in diminishing absorption is the same as found by Fischer for gelatin and fibrin, namely: chloride, tartrate, phosphate. That the relative position of the curves for the four salts is not the same for all concentrations may or may not be significant. We do not think the matter due to experimental error. There is undoubtedly a very important relation between the exact concentration of the acid and the inhibiting effect at different concentrations, of the salts. Of special interest is the fact that glyocoll behaves like a salt in reducing the swelling of gluten in acid solution. The effect, however, is less marked than with the different salts studied.

A series of photographs will help to make evident the significant differences in the swelling of gluten under different conditions.



Plate I.

Plate I shows the lactic acid series (a) of Table I. Beaker 1 contains distilled water. Beakers 2 to 7 contain lactic acid in concentrations from 0.002 *N* to 0.1 *N* as shown in Table I. The difference in size of the discs in distilled water and in the different concentrations of acid is plainly evident.

Plate II shows a 0.005 *N* lactic acid series, to which has been added varying concentrations of K_2HPO_4 as in Table V. Beaker 1 contains



Plate II.

0.01 *N* lactic acid. Beakers 2 to 7 contain 0.01 *N* lactic acid with K_2HPO_4 varying in concentration from 0.01 *M* to 0.4 *M*. The increasing antagonistic effect of the salt with increasing concentration is very apparent.

TABLE VI.

| A. Original wt. of discs. | | B. Wt. of discs after 2 hrs. in acid. | | Conc. of acid. | C. Wt. of discs after transference to 0.1 <i>N</i> K_2HPO_4 for 1 hr. | |
|------------------------------|------|---|------|-------------------|--|------|
| a. | b. | a. | b. | | a. | b. |
| 1.39 | 1.23 | 1.41 | 1.20 | No acid | 1.14 | 0.95 |
| 1.30 | .26 | 3.21 | 2.89 | 0.002 <i>N</i> | .18 | .16 |
| 1.33 | .22 | 3.43 | 3.54 | 0.005 <i>N</i> | .22 | .10 |
| 1.39 | .28 | 3.57 | 3.67 | 0.01 <i>N</i> | .27 | .17 |
| 1.42 | .24 | 3.92 | 3.67 | 0.02 <i>N</i> | .30 | .14 |
| 1.29 | .27 | 3.90 | 3.85 | 0.04 <i>N</i> | .17 | .15 |
| 1.29 | .29 | 3.95 | 3.69 | 0.1 <i>N</i> | .21 | .24 |
| 1.31 | .29 | 3.69 | 3.56 | 0.2 <i>N</i> | .28 | .26 |
| 1.31 | 1.30 | 3.52 | 3.46 | 0.5 <i>N</i> | .35 | .35 |

Table VI shows the reversible nature of water absorption by gluten. There are shown in Col. A the original weights of two series of gluten discs, and in Col. B their weights after remaining two hours in acetic acid solutions varying from 0.002 *N* to 0.5 *N*. In Col. C are given the weights of the same discs after remaining one hour in 0.1 *N* dipotassium phosphate solution. These experiments show how the discs, after taking up water in the acid solutions to twice their original weight or more, give up the water in the salt solution. Not only do they reassume their original weight, but their original appearance and physical properties as toughness and elasticity as well.

TABLE VII.—EFFECT OF TEMPERATURE ON WATER ABSORPTION.

| Solution. | Wt. of water absorbed in g. per g. of moist gluten. | |
|------------------------------|--|------|
| | 24°. | 39°. |
| In water..... | 0.06 | 0.09 |
| In 0.01 <i>N</i> HCl..... | 1.47 | 2.01 |
| In 0.01 <i>N</i> lactic..... | 1.65 | 2.66 |
| In 0.01 <i>N</i> acetic..... | 1.68 | 2.79 |

Table VII is introduced to show the effect of temperature on the absorption of water by gluten. It shows that gluten swells the more in acid solutions the higher the temperature.

TABLE VIII.—0.01 *N* LACTIC ACID WITH VARYING AMOUNTS OF FLOUR AND BRAN EXTRACTS.

| 0.01 <i>N</i> lactic acid cont. extract from flour. | Water abs. in g. per g. of moist gluten. | 0.01 <i>N</i> lactic acid cont. extract from bran. | Water abs. in g. per g. of moist gluten. |
|---|--|--|--|
| No extract | 2.23 | No extract | 1.48 |
| 0.625 g. per 100 cc. | 2.16 | 0.625 g. per 100 cc. | 1.12 |
| 1.25 g. per 100 cc. | 1.81 | 1.25 g. per 100 cc. | 1.02 |
| 2.50 g. per 100 cc. | 1.47 | 1.87 g. per 100 cc. | 0.91 |
| 5.00 g. per 100 cc. | 1.25 | 2.50 g. per 100 cc. | 0.82 |
| | | 4.75 g. per 100 cc. | 0.33 |

TABLE IX.—0.01 *N* LACTIC ACID WITH VARYING AMOUNTS OF CANE SUGAR.

| Conc. of sugar solution. | Water abs. in g. per g. of moist gluten. |
|--------------------------|--|
| None | 1.75 |
| 0.1 <i>M</i> | 1.41 |
| 0.2 <i>M</i> | 1.54 |
| 0.5 <i>M</i> | 1.42 |
| 1.0 <i>M</i> | 0.71 |
| 1.5 <i>M</i> | 0.28 |

Table VIII shows that water extracts of flour and bran reduce the swelling of gluten in acid solutions. Their effect is similar to, though not as marked, as the effect of neutral salts.

Table IX shows that nonelectrolytes such as cane sugar are comparatively ineffective in reducing the swelling of gluten in acid solutions except in high concentrations. Fischer finds the same for gelatin and sugar solutions.

The experiments described in this paper show that the mixture of vegetable proteins which comprises wheat gluten behaves in a manner entirely analogous to the animal colloids as studied by Fischer and others. Moist gluten absorbs water from acid solutions and the amount of absorption varies with the kind and concentration of the acid. The presence of neutral salts retards water absorption by gluten, and in the higher concentrations of salt may even cause loss of water from moist gluten. Gluten which has taken up water in an acid solution loses water and regains its original physical properties when placed in a salt solution. The nonelectrolytes are much less effective than electrolytes in inhibiting the swelling of gluten in acid solutions. These experiments therefore contribute to the important problem of the mechanism of water absorption and secretion by living plants which in animals has been proved by Fischer to be essentially a colloid phenomenon.

The facts brought out in our experiments, coupled with those of Wood and Hardy, are also of importance in relation to certain theoretical and practical problems of milling and baking. This topic we propose to discuss in a forthcoming bulletin from the Nebraska Experiment Station.

We would here express to Dr. Martin H. Fischer of the University of Cincinnati our appreciation of his interest in this work.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY,
No. 248.]

STUDIES ON AMYLASES. X. COMPARISON OF CERTAIN PROPERTIES OF PANCREATIC AND MALT AMYLASE PREPARATIONS.

By H. C. SHERMAN AND M. D. SCHLESINGER.

Received February 23, 1915.

Notwithstanding the numerous investigations of recent years, no consensus of opinion has yet been reached as to how far the enzymes of similar activity, but different origin, are to be regarded as distinct substances.

The best amylase preparations obtained in this laboratory from the pancreas and from malt are found to be very similar in physical properties and in chemical nature, so far as shown by their qualitative reactions, the percentage of nitrogen which they contain, and the distribution of this nitrogen among the different types of amino-acid radicals. That they are nevertheless not identical appears to be established by certain differences in their behavior.

Activity.

Optimum Reaction.—Perhaps the most noticeable difference between these two enzymes is that malt amylase is most active in an acid, and pancreatic amylase in an alkaline solution.

Electrometric measurements recently made in this laboratory¹ have shown that the optimum acidity for malt amylase (saccharogenic action in 30 minutes at 40°) is P_H^+ 4.2 to 4.6, the optimum action being found at this point, whether the activating agent be a strong acid, a weak acid, or an acid phosphate. Solutions of this hydrogen ion concentration give a distinct (but not strong) red reaction with azolitmin, while methyl orange gives an orange color.

Exact measurements of the optimum alkalinity for pancreatic amylase have not yet been made, but the reaction which has seemed best in the regular testing of these preparations has been that obtained by the use of 7 cc. of 0.02 *M* disodium phosphate and 5 cc. of *M* sodium chloride in each 100 cc. of previously neutral 2% starch. Such a solution gives a distinct (but not strong) blue reaction with azolitmin and is colorless with phenolphthalein. According to Sørensen this indicates a P_H^+ of 8.0 to 8.5. We hope soon to confirm this by the electrometric method.

Diastatic Power.—When each is tested in the presence of its proper activating electrolyte but with time, temperature, and substrate the same, the diastatic powers of the best preparations thus far obtained are fully twice as high for the pancreatic as for the malt amylase. The most active preparations of pancreatic amylase show diastatic powers around

¹ Sherman and Thomas, *THIS JOURNAL*, 37, 623 (1915).

4000 (new scale) corresponding to Lintner figures of about 6000, which means that the enzyme preparation forms 10,000 times its weight of maltose in 30 minutes at 40°. The most active preparations of malt amylase yet obtained showed powers of 1570 (new scale) corresponding to a power of about 2350 on Lintner's scale, and forming about 4000 times its weight of maltose in 30 minutes at 40°.

The foregoing statements refer in all cases to the relative amounts of reducing sugar formed under the action of the enzyme (saccharogenic activity or saccharogenic power). That the amylolytic activity, as usually measured by determining the relative amount of starch *all* of which is digested under specified conditions into products giving no blue or violet color with iodine, runs approximately parallel with the saccharogenic power among amylase preparations from the pancreas and not among the corresponding preparations from malt, constitutes another interesting point of difference between the two amylases. This point was discussed recently¹ and therefore need not receive further attention here.

Proteolytic Activity.—Another pronounced difference between our amylase preparations from the two sources is that in those from pancreatin, proteolytic activity, as shown in the digestion both of casein² and of gelatin,³ was concentrated with the concentration of the diastatic power, whereas in our purified malt amylase preparations we have not yet succeeded in demonstrating any proteolytic activity.

Deterioration.—Our pancreatic and malt amylase preparations also differ strikingly in the rate at which their solutions lose diastatic power on standing.⁴ Under the conditions obtaining in our experiments, malt amylase is much the more stable in pure water solution, while pancreatic amylase is the more stable in 50% alcohol and remains active longer than the malt amylase when allowed to act upon starch.

The following are illustrative of numerous experimental data on which the foregoing statement is based:

Pancreatic and Malt Preparations in Solution at Ice-box Temperature.—The results of deterioration experiments with commercial pancreatin and malt extract, with purified amylases of high activity, and with intermediate products, are shown in Table I. (When a value is given in parenthesis with the designation of the preparation at the head of a column, it represents the original diastatic power of the preparation when first obtained.)

¹ THIS JOURNAL, 35, 1784-90 (1913).

² *Ibid.*, 34, 1109-10 (1912).

³ Wahl, *Orig. Com. 8th Intern. Congr. Appl. Chem.*, 14, 215 (1912).

⁴ The rate of deterioration when kept in the dry state varies too much with conditions to permit definite conclusions to be drawn from the data at hand. On the whole, the pancreatic preparations appear to have retained their diastatic power rather better than those from malt, when kept dry at the same temperature.

TABLE I.—DETERIORATION OF PANCREATIC AND MALT AMYLASES IN WATER AT 5-10°.

| | From pancreas. | | | From malt. | | | | | | | | |
|---|------------------------|-----------------|--------------------------|--|---------------------------|--|----------------------------|---------------------------|-----------------------------|---------------------------|--|--|
| Diastatic powers found when solutions were tested as below. | Pancreatin 5 (400). | Preparation 21. | Preparation 60 (3560) | Malt extract. Preparation 101 (780). | Preparation 53 (1220). | Preparation 53 with toluene. Preparation 53 with tri- sol. | Preparation 13B (1060). | Preparation 112 (900). | Preparation 111B (1470). | Preparation 52 (1470). | | |
| At once..... | 400 | 2150 | 3560 | 5.5 240 | 490 | 480 490 | 570 | 900 | 1150 | 1470 | | |
| After 1 hour..... | .. | .. | 2200 | .. | .. | .. | .. | .. | .. | .. | | |
| After 3 hours..... | .. | 1520 | 1290 | .. | .. | .. | .. | .. | .. | .. | | |
| After 24 hours..... | 380 | 1440 | 0 | 6.1 .. | 500 | .. | .. | .. | 1060 | 1230 | | |
| After 48 hours..... | 370 | 1080 | .. | 5.3 .. | .. | .. | .. | 900 | 1050 | .. | | |
| After 72 hours..... | 265 | .. | .. | 5.0 .. | .. | .. | .. | .. | .. | .. | | |
| After 4 days..... | .. | .. | .. | 4.9 260 | .. | .. | 410 | .. | .. | .. | | |
| After 6 days..... | .. | .. | .. | 4.7 260 | 440 | .. | 440 | .. | .. | .. | | |
| After 8 days..... | .. | .. | .. | .. | 440 | 440 380 | .. | .. | .. | .. | | |
| After 13 days..... | .. | .. | .. | .. | 430 | 430 330 | .. | .. | 1150 | .. | | |
| After 14 days..... | .. | .. | .. | .. 250 | 380 | 420 310 | 190 | .. | .. | .. | | |
| After 17 days..... | .. | .. | .. | .. 260 | .. | .. | 0 | .. | .. | .. | | |
| After 24 days..... | .. | .. | .. | .. 260 | .. | 340 260 | .. | .. | .. | .. | | |
| After 27 days..... | .. | .. | .. | .. 260* | 0 | 320 230 | .. | .. | .. | .. | | |

It will be seen from the table that, whether crude or purified material be compared, the malt amylase is much the more stable in cold water solution (5° to 10°). The solution of commercial pancreatin lost one-third of its activity in 3 days, while the malt extract showed a smaller loss after 6 days, its activity when 3 days old being nearly equal to that when freshly prepared. The highly purified pancreatic amylase (No. 60) lost all of its activity within 24 hours, while the highly purified malt amylase preparation (No. 52) lost less than one-fifth of its activity under the same conditions. Pancreatic preparation No. 21 (having about three-fifths the activity of No. 60) lost half its diastatic power in 48 hours, while malt preparation No. 112 (having three-fifths the activity of No. 52) showed no appreciable loss in the same length of time.

In the case of the pancreatic amylase it is plain that the rapidity of deterioration is proportional to the purity of the preparation and, in general, a similar relationship appears among the malt preparations. The latter, however, show irregular results, possibly because they are less homogeneous products, and probably also because the malt amylase solutions retain their activity so long that (when no antiseptics are used) there is sometimes bacterial action even at the low temperature of these observations. More experiments upon the influence of antiseptics are contemplated.

Both the great stability of the malt amylase solutions as compared

* In this case only, the activity was studied beyond the 28th day. The last observation was taken on the 53d day and showed a diastatic power of 230, indicating that in this case there was little loss of activity in over seven weeks.

with those of pancreatic amylase, and the fact that the former may show increased activity after standing for some time may be due, in part at least, to the presence in the malt preparations of some malt albumin which retards hydrolysis of the enzyme when in solution, or possibly protects it from deterioration in some other way. This point was discussed in our last paper.

Effect of Heat upon Dry Enzyme.—It is well known that enzymes, when dry, are much more stable at high temperatures than are their solutions. In our experience, however, it has not been found possible to heat the dry enzyme preparations at 100° without considerable loss of diastatic power. Pancreatic amylase preparation 35, which originally had a power of 3450, showed after heating for one hour at 100° a power of 1020. Malt amylase preparation 111B, which originally had a power of 1150, showed after the same treatment a power of 510. Thus the heating destroyed about two-thirds of the activity of the pancreatic and about one-half the activity of the malt amylase.

Statements in the literature to the effect that dry enzymes can be heated at 100° "without loss of activity," are probably based (for the most part at least) upon qualitative experiments and should perhaps be construed to mean "without becoming inactive," *i. e.*, the loss of activity is only partial and in qualitative experiments would very likely not be apparent.

Effect of Temperature and of Activating Salts upon Deterioration of Pancreatic and Malt Amylase in Water Solution.—The effect of temperature upon the rate of deterioration of diastatic power in commercial and purified amylase preparations, and the relative stability of these preparations in pure water solution and in the presence of "activating" salts, are shown in Table II. It will be seen that in pure water solutions the deterioration is always more rapid the warmer the solution. For both pancreatic and malt amylase the deterioration is more rapid the purer the enzyme. Pancreatic amylase in water solution is to an important extent preserved from deterioration by the presence of the mixture of salts which is favorable to its action (sodium chloride and secondary sodium phosphate); on the other hand, purified malt amylase may deteriorate more rapidly in the presence of its "activating" salt (primary sodium phosphate) than in pure water, probably because the deterioration is due to an hydrolysis of the enzyme, which is accelerated by increasing the hydrogen ion concentration of the solution. As will be more fully explained beyond, the enzyme is, in these deterioration experiments, dissolved in the water or salt solution in larger quantity (concentration) than would be used in determinations of diastatic power or in long-digestion experiments, since portions of the deteriorating solution must be

withdrawn from time to time in order to determine the proportion of enzyme still remaining active.

TABLE II.—DETERIORATION AT DIFFERENT TEMPERATURES IN WATER WITH AND WITHOUT "ACTIVATING" SALTS.

| Diastatic power found when solution had stood at temperature and for time given below. | From pancreas. | | | | | | | From malt. | | | | | | |
|--|---|--|--|---|--|--------------------------------------|--------------------------------------|---|---------------------|----------------------|----------------------|-------------------------------|---------------------------------------|---------------------------------|
| | Pancreatin 4 in pure water at 20° to 25°. | Pancreatin 4 with NaCl and NaH ₂ PO ₄ at 20° to 25°. | Preparation 21 in pure water at 3° to 10°. | Preparation 21 in pure water at 20° to 25°. | Preparation 21 with NaCl and NaH ₂ PO ₄ at 20° to 25°. | Preparation 57 in pure water at 25°. | Preparation 57 in pure water at 40°. | Prep. 60 with NaCl and NaH ₂ PO ₄ at 40°. | Malt extract at 7°. | Malt extract at 23°. | Malt extract at 40°. | Prep. 67 in pure water at 7°. | Prep. 67 in pure water at 20° to 25°. | Prep. 139 in pure water at 40°. |
| 15 mins. | ... | ... | ... | ... | ... | 3120 | 1230 | ... | 5.5 | 5.7 | 5.7 | ... | ... | ... |
| 20 mins. | 133 | 189 | ... | 1240 | 2115 | ... | ... | ... | ... | ... | ... | ... | ... | ... |
| 30 mins. | ... | ... | ... | ... | ... | 2430 | ... | 3270 | ... | ... | ... | ... | ... | ... |
| 45 mins. | ... | ... | ... | ... | ... | 1740 | 270 | ... | ... | ... | ... | ... | ... | ... |
| 60 mins. | 111 | ... | ... | 1020 | ... | 1610 | ... | 2850 | ... | ... | 5.1 | ... | ... | ... |
| 2 hrs. | 81 | ... | ... | 675 | ... | ... | 0 | 1970 | ... | ... | ... | ... | ... | 800 770 |
| 3 hrs. | 57 | 165 | 1520 | 535 | 1720 | 390 | ... | ... | ... | ... | 5.0 | 870 | 930 | ... |
| 18 hrs. | ... | ... | ... | ... | ... | ... | ... | 0 | ... | ... | ... | ... | ... | ... |
| 24-27 hrs. | 0 | 124 | 1440 | 0 | 1200 | 0 | ... | ... | 6.1 | 5.3 | 3.9 | 870 | 870 | 780 480 |
| 2 days | ... | ... | 1080 | ... | ... | ... | ... | ... | 5.3 | 5.0 | 2.1 | ... | ... | 750 390 |
| 3 days | ... | ... | ... | ... | ... | ... | ... | ... | 5.0 | ... | 0.6 | ... | ... | 750 360 |
| 4 days | ... | ... | ... | ... | ... | ... | ... | ... | 4.9 | 4.7 | 0.2 | 870 | 600 | 750 300 |
| 5 days | ... | ... | ... | ... | ... | ... | ... | ... | 4.9 | 4.3 | 0 | 830 | 490 | 730 290 |
| 6 days | ... | ... | ... | ... | ... | ... | ... | ... | 4.7 | 4.1 | ... | 830 | 230 | 560 290 |

In water solutions the deterioration is more strikingly accelerated by rise of temperature in the case of the pancreatic than of the malt amylase.

A further comparison of the rate of deterioration of pancreatic preparations of different degrees of purity, when kept in pure water at room temperature, may be summarized briefly as follows:

| | | | | | |
|--|------|------|------|------|------|
| Initial diastatic power..... | 3430 | 2000 | 1185 | 425 | 150 |
| Percentage of initial power lost in 20 minutes.... | 45.5 | 32.5 | 25.8 | 19.0 | 11.3 |
| Percentage of initial power lost in 3 hours..... | ? | 73.3 | 72.3 | 62.5 | 62.0 |

All of these solutions became entirely inactive within 24 hours. These data seem sufficiently suggestive to warrant fuller investigation at accurately controlled temperatures.

Behavior in the Presence of Substrate.—In marked contrast to their deterioration in water solutions (with and without activating salts), is the behavior of the two amylases in the presence of a sufficient amount of starch to test the duration of their activity, when allowed to come in contact with their substrate, and the maximum amount of reducing sugar calculated as maltose which the enzyme can form in relation to its own weight. In Table III are shown the data obtained when different amylase preparations were allowed to act upon many times their weight of soluble starch, the latter being usually in the form of a 1% solution. Toluene

TABLE III.—LONG-DIGESTION EXPERIMENTS WITH SOLUBLE STARCH AT 40°.

| Enzyme. | Initial relation of enzyme to starch, 1. | Color reaction with iodine, and maltose formed (enzyme to maltose as 1 to figure given below). | | | | |
|--|--|--|-------------|------------|------------|---|
| | | 24 hours. | 48 hours. | 72 hours. | 96 hours. | 120 hours. 144 hours. 168 hours. 192 hours. |
| Malt amylase preparation No. 52. | 25,000 | Red-violet | Violet-red | Violet-red | Violet-red | Violet-red |
| | 17,000 | | 17,000 | 17,000 | | |
| | 50,000 | | Red-violet | Red-violet | | |
| | | Blue | 34,000 | 34,000 | | |
| | 75,000 | 40,000 | Violet-blue | Violet | | |
| | | Blue | 49,000 | 50,000 | | |
| | 150,000 | 64,000 | Blue | Blue | | Blue |
| | | Blue | 75,000 | | | .. |
| | 300,000 | 90,000 | Blue | Blue | | Blue |
| | | Blue | 93,000 | 93,000 | | .. |
| Pancreatic amylase, preparation No. 34. | 1,000,000 | 76,000 | Blue | | | |
| | | 76,000 | 76,000 | | | |
| | | Red | Colorless | | | |
| | 400,000 | 182,000 | 211,000 | | | |
| | | Violet-red | Red | Colorless | | |
| | 800,000 | 273,000 | 379,000 | 455,000 | | |
| | | Blue | Red-violet | Red | Orange | |
| | 1,000,000 | 203,000 | 305,000 | 408,000 | 470,000 | |

| | | | | | |
|--|------------------------|-----------------------|--------------------------|----------------------|----------------------|
| Pancreatic amylase preparation No. 50..... | 500,000 | Orange-red 211,000 | Colorless 276,000 | | Colorless 292,000 |
| | | Violet-red | Yellow-orange | | Colorless |
| | 1,000,000 | 356,000 | 440,000 | | 516,000 |
| | | Blue | Red-violet | Red | Colorless |
| | 1,000,000 ¹ | | | 388,000 | |
| Pancreatic amylase preparation No. 57..... | 1,000,000 | | Orange-yellow 581,000 | Colorless 581,000 | Colorless 596,000 |
| | | | Violet-red | Light orange | Colorless |
| | 2,000,000 ² | | 823,000 | 950,000 | 1,200,000 |
| | | | Violet-red | Light orange | Colorless |
| | 2,000,000 ³ | | 822,000 | 950,000 | 1,165,000 |

1. In this case the digestion mixture had one-half the usual concentration of salt and phosphate.

: In this experiment a 2% starch solution was used.

³ In this experiment a 4% starch solution was used.

N. B. In all except these three cases the digestion mixture contained 1% of starch and the usual concentration of electrolyte; primary phosphate for malt amylase, secondary phosphate and sodium chloride for pancreatic amylase.

was used as antiseptic in all these cases. At intervals of about 24 hours, portions of each solution were withdrawn for testing with iodine and for the determination of maltose. The colors obtained in the iodine test, and the number of times its weight of maltose which the enzyme had formed up to the time of the test, are given together in the table.

On the scale of diastatic power in use in this laboratory,¹ pancreatic amylase preparation 57 showed a power of 3700 (in the air-dry condition, corresponding to about 4000 for the dry substance) which is a higher activity than we had previously² observed. Pancreatic preparation 50 had a power of 3200, and preparation 34 a power of 3430 when freshly prepared, and of 2560 at the time of the experiment recorded in Table III. Malt amylase preparation 52 had a power of 1470 when freshly prepared, but at the time of the "long-digestion" experiments recorded in the table it had been kept in powder form for some months and its diastatic power had fallen to 980. This malt preparation, as originally tested, bears about the same relation in diastatic power to the best malt amylase yet obtained, which pancreas preparation 50 bears to 57; in relative activity at the time these tests were made it is similarly comparable to pancreas preparation 34. A comparison of malt preparation 52 with pancreas preparations 50 and 34, as regards duration of activity and relation between initial and total activity, seems therefore logical and brings out the following interesting difference:

Malt amylase preparation 52 produced 2450 times its weight of maltose in 30 minutes, in 48 hours it had produced 93,000 times its weight of maltose, and thereafter it showed no activity.

Pancreatic amylase preparation 50 formed 8000 times its weight of maltose in 30 minutes; 440,000 in 48 hours; 516,000 in 96 hours.

Pancreatic preparation 34 under similar conditions formed 6450 parts of maltose in 30 minutes; 305,000 in 48 hours; 408,000 in 72 hours; 470,000 in 96 hours.

Thus, while the malt amylase had expended its entire activity within 48 hours and produced in all about 38 times as much maltose as it formed in the first 30 minutes, the pancreatic amylases in the same circumstances (presence of large excess of substrate) continued active for 72 to 96 hours and formed, respectively, in the first 48 hours, 55 and 48 times, and in all, 65 and 73 times as much maltose as in the first 30 minutes.

Thus the influence of the substrate in protecting the enzyme from deterioration in aqueous solution was much greater in the case of the pancreatic than of the malt amylase.

Direct comparison of the data for the malt amylases, as given in Table II,

¹ Sherman, Kendall, and Clark, *THIS JOURNAL*, 32, 1082-85 (1910); Sherman "Methods of Organic Analysis," 2nd Edition, 117-118.

² *THIS JOURNAL*, 33, 1202 (1911).

with those in Table III might lead to the impression that this enzyme deteriorates faster in the presence of its substrate, but no such interpretation is justified, because the ratio of water to enzyme is about 1000 times as great in the latter experiments as in the former. It therefore seemed desirable, in the case of the malt amylase, to compare the rate of deterioration at the different dilutions, notwithstanding the fact that only approximate results can be obtained from deterioration experiments in which the ratio of water to enzyme is of such magnitude as obtains in the long-digestion experiments. The data of such a comparison are shown in Table IV.

TABLE IV.- INFLUENCE OF DILUTION UPON DETERIORATION OF MALT AMYLASE AT 40°.

| Diastatic power found after solution had stood as indicated below. | Malt amylase preparation No. 139 (960). | | |
|---|---|--|--|
| | 10 mgs. in 100 cc. pure water (1:10,000) at 40°. | 0.01 mg. in 100 cc. pure water (1:10,000,000) at 40°. | 0.01 mg. in 100 cc. water containing the "optimum" concentra- tion of NaH_2PO_4 at 40°. |
| After 15 minutes..... | 760 | 500 | 500 |
| After 2 hours..... | 760 | 200 | 200 |
| After 24 hours..... | 700 | 100 | 100 |
| After 48 hours..... | 630 | 0 | 0 |
| After 4 days..... | 600 | | |
| After 7 days..... | 270 | | |
| After 10 days..... | 100 | | |

From these data it will be seen that the malt amylase deteriorated as much in one day at a dilution of 1:10,000,000 as in 10 days at a dilution of 1:10,000. Parallel experiments with pancreatic amylase are impracticable because of its much more rapid deterioration in water.

The significance of the different behavior of the two amylases in water solution, and of the influence of the substrate upon the rate at which the enzyme loses its diastatic power will be discussed further on in this paper after certain chemical and physical characteristics have been described.

Deterioration in Alcohol at Different Temperatures.—Whereas in pure water solutions the pancreatic amylase deteriorates much more rapidly than malt amylase, this is not the case when the preparations are dissolved in 50% alcohol, as will be seen from Table V.

From the data in Table V it is evident that the alcohol solutions of both the amylases are much more stable at low temperature (5° to 10°) than at the ordinary room temperature of about 23°.

While not enough observations have been made to permit detailed comparison, it appears that, as in the case of water solutions, the purer the enzyme the more rapid its deterioration.

Comparing the data of Tables I, II, and V it will be seen that, at similar temperatures, purified pancreatic amylase is more stable in 50% alcohol than in water, whereas purified malt amylase is more stable in water than in 50% alcohol.

TABLE V.—DETERIORATION OF AMYLASES IN 50% ALCOHOL AT DIFFERENT TEMPERATURES.

| Diatstatic power found when solution had stood as in- dicated below. | From pancreas. | | | | | From malt. | | | |
|---|----------------------------|-----------------------------|--------------------------|---------------------------|-------------------------------|------------------------|-------------------------|------------------------------|-------------------------------|
| | Pancreatin No. 5 at 5°. | Pancreatin No. 5 at 23°. | Preparation F2 at 5°. | Preparation F2 at 23°. | Preparation No. 21 at 23°. | Malt extract at 7°. | Malt extract at 23°. | Preparation No. 67 at 7°. | Preparation No. 67 at 23°. |
| After 5 minutes..... | 400 | 330 | 550 | 550 | 2000 | 5.4 | 5.4 | (800) | 570 |
| After 3 hours..... | ... | ... | ... | ... | .. | ... | ... | 705 | 490 |
| After 20 hours..... | ... | ... | 540 | 335 | 1350 | ... | ... | ... | ... |
| After 24 hours..... | 385 | 290 | 540 | ... | 1200 | 5.4 | 5.1 | 510 | 66 |
| After 48 hours..... | 370 | 290 | ... | 260 | .. | 4.9 | 4.4 | ... | ... |
| After 3 days..... | 265 | 150 | ... | ... | ... | ... | 3.3 | ... | ... |
| After 4 days..... | ... | ... | ... | ... | .. | 4.7 | 2.7 | 350 | 0 |

Chemical Composition and Color Reactions.—Our preparations of both pancreatic and malt amylase are essentially proteins in that they show the typical color reactions,¹ contain 15 to 16% of nitrogen,² and on hydrolysis are resolved into amino acids. Determinations, by the Van Slyke method, of the distribution of the nitrogen among the different types of amino acid radicals show³ that these preparations contain the same forms of nitrogen in about the same proportions as found in such typical proteins as casein and edestin.

Amylase preparations from both sources react as ordinary proteins in the Millon, xanthoproteic, tryptophan, and biuret tests.

Physical Properties.—The amylases from malt and from pancreas are both soluble in water and in 50% alcohol; insoluble in strong alcohol or acetone. In general, our preparations from malt are less readily soluble in water or in diluted alcohol than are those from pancreas.

Solutions of preparations from both sources give similar colloidal appearance under the ultramicroscope, but some isolated observations upon one of our malt preparations suggest that a part at least of the colloidal appearance may be due to material other than the active enzyme, possibly inactive protein formed by deterioration of the enzyme during purification as explained later in this paper. We hope to make a more systematic series of ultramicroscopic observations in the near future.

In diffusion experiments both amylases are retained either by parchment paper or by collodion membrane. Occasionally the dialyzate shows some diastatic power, but this is so slight in comparison with that of the dialyzing solution, and so irregular in its occurrence, that it may readily be due to imperceptible defects in the membrane. (See also description of dialysis experiments beyond.)

¹ THIS JOURNAL, 33, 1203 (1911); 35, 1622 (1913).

² *Ibid.*, 34, 1106 (1914); 37, 643 (1915).

³ *Ibid.*, 35, 1792-4 (1913).

Coagulation.—One per cent. solution of either amylase when heated above 50° yields a precipitate of coagulated albumin. This coagulum gives in both cases a blue-violet biuret reaction. The filtrate from this coagulum gives a biuret reaction which is rose-red in the case of the pancreatic, and violet-red in the case of the malt preparation. Thus both of these amylase preparations resemble that of Osborne in yielding coagulable albumin and a proteose or peptone, the latter apparently representing a product of somewhat more advanced hydrolysis in the case of pancreatic than of malt amylase.

In order to study further the change which takes place on coagulation, 200 mg. of a malt amylase preparation¹ (equivalent to 0.1836 g. of dry ash-free substance) were dissolved in 20 cc. of water and heated gradually in a beaker with constant stirring. Between 50° and 55° , coagulation took place and the coagulated protein flocculated well, leaving a clear solution. The coagulum after washing and drying weighed 0.1136 g. (61.8% of the dry weight of the sample) and contained 16.1% of nitrogen. The filtrate, containing 0.0700 g. of the original (dry ash-free) substance yielded 0.00959 g. nitrogen, showing 13.7% of nitrogen in the noncoagulable fraction of the enzyme preparation.

In a parallel experiment with pancreatic amylase, 300 mg. of preparation 60, equivalent to 0.2640 g. dry, ash-free substance, was dissolved in 30 cc. of water and heated as above. Coagulation occurred between 50° and 55° . The coagulum after washing and drying weighed 0.0306 g. (11.6% of the original dry weight) and showed 16.9% of nitrogen. The uncoagulable ash-free material of the filtrate weighed 0.2334 g. and showed 14.9% of nitrogen.

Dialysis.—Under the heading of activity, we have described above the rapid deterioration of pancreatic amylase in water solution at room temperature, and the relative stability of malt amylase under the same conditions. In the preceding paper² we have shown that the most serious loss of diastatic power encountered in the purification of malt amylase is that due to its deterioration during dialysis, and have suggested that this deterioration may be due to the removal through the dialyzing membrane of a portion of the proteose (or peptone) fraction of the enzyme.

The following experiments were designed to test this view:

1. A solution of 20 mg. of a purified preparation of malt amylase (Preparation 117; power 1070, new scale) in 50 cc. water was dialyzed against 500 cc. water at a temperature of 5° to 10° for 24 hours, at the end of which time the activity of the solution corresponded to a power of 190 (new scale), *i. e.*, four-fifths of the power was lost. The dialyzate alone showed almost no activity, 50 cc. forming only enough maltose to

¹ Preparation 111B described in the preceding paper.

² THIS JOURNAL, 37, 643 (1915).

reduce 3 mg. of cuprous oxide; but 50 cc. of the same dialyzate, when added to 0.5 cc. of the dialyzed solution, increased the activity of the latter to the extent of producing enough additional maltose to reduce 15 mg. of cuprous oxide. This corresponds to a restoration of about one-thirtieth of the power which the enzyme had lost during the dialysis. As a difference of one-thirtieth of the total power is hardly larger than the experimental errors involved in such work we should not attach much importance to this apparent restoration of a part of the lost activity, except for the fact that a similar result was again observed in the subsequent trial in which the experimental conditions were quite different. At any rate, it is plain that only a small part of the lost power was restored to the dialyzed solution by the addition of the dialyzate, indicating that, when the two constituents of the enzyme are separated by dialysis, at least one of them undergoes some further change which prevents the regeneration of more than a small fraction of the enzyme when the two solutions are subsequently mixed.

2. A solution of 200 mg. of preparation 111B (power when freshly prepared 1470, new scale, at time of this experiment 1050, new scale) in 20 cc. water was dialyzed against 200 cc. water at a temperature of 5° to 10° for 48 hours, at the end of which time the activity of the solution corresponded to a power of 750 (new scale), *i. e.*, about 30% of the power was lost. That the loss here is less than in the preceding experiment is doubtless due to the much lower ratio of water to enzyme. In this case the dialyzate showed measurable activity, about 6% of the total initial power, and again the mixing of the dialyzate with the dialyzed solution resulted in a small but appreciable restoration of power, somewhat greater than in the preceding experiment, as would be expected in view of the lower ratio of water to enzyme.

The dialyzate was concentrated by evaporation and found to give a distinct biuret reaction which was notably pinker in color than that given by the original enzyme solution. The same amount of (boiled down) dialyzate which gave this biuret reaction failed to give any coloration with triketohydrindene hydrate (ninhydrin).

All of our observations upon the properties of the pancreatic and malt amylase preparations, including their behavior in solution in the presence and absence of substrate and in dialysis and coagulation, appear to be consistent with the following hypothesis as to their chemical nature, based on that suggested by Osborne in 1896:

Pancreatic and malt amylases, although not identical substances, may each be regarded as a complex protein consisting of an albumin fraction and a proteose (or peptone) fraction. In either case, when the enzyme is heated in water solution these parts are separated by hydrolysis and the

albumin fraction coagulated. Probably the same sort of hydrolysis takes place to some extent at room temperatures, or even in cooler solutions.

In the case of malt amylase this cleavage into albumin and proteose appears to be an easily reversible reaction, so that when simply standing in water solution the enzyme molecule is in equilibrium with its cleavage products and there is no rapid destruction of the enzyme by the water at ordinary temperature. If, however, such a water solution is placed in a dialyzer it deteriorates¹ much more rapidly, probably because of the removal of the dialyzable cleavage product. Since the diastatic power thus lost is only to a slight extent restored by subsequently mixing the dialyzate with the dialyzed solution, it appears probable that the dialyzable proteose fraction, when separated from the albumin fraction by the dialyzer membrane and exposed to the action of a relatively large amount of water, undergoes some further cleavage or other change which is evidently not readily reversible.

In the case of pancreatic amylase it would seem that a similar cleavage of the enzyme into an albumin and a proteose or peptone takes place, but that this action is much less readily reversible than in the case of malt amylase, so that on standing in water solution the pancreatic amylase deteriorates very much more rapidly. The fact that the boiled-down solution of the noncoagulable cleavage product gives a pinker color with the biuret reagent in the case of pancreatic than of malt amylase, suggests that the proteose fraction of the enzyme may more readily undergo further cleavage in the case of pancreatic amylase and that this may account for the fact that the enzyme is not (as in the case of malt amylase) protected from rapid deterioration by establishing equilibrium with its primary cleavage products.

Probably in both cases the amylolytic action involves first a combination of the amylase with the starch, and while in such combination the labile constituent of the enzyme is protected from destructive change. With pancreatic amylase this has the effect of greatly prolonging the "life" of the enzyme which would otherwise undergo rapid hydrolytic destruction as outlined in the preceding paragraph. On the other hand, with malt amylase the labile constituent is protected by the readily reversible character of the primary hydrolysis which results in the establishment of a condition of equilibrium in which most of the enzyme exists intact, so that there is only a very slow deterioration, even in the absence of the substrate, and the influence of the latter upon the duration of activity of the enzyme is therefore not readily demonstrable.

¹ Since in all of our work the activating salts are added to the optimum concentrate at the time of determining diastatic power, the deterioration cannot be attributed simply to the removal of electrolytes.

Summary.

The purified amylase preparations obtained from the pancreas and from malt are similar in many respects but are not identical substances.

Both are amorphous nitrogenous substances soluble in water or in 50% alcohol, but insoluble in concentrated alcohol or acetone.

Both show typical protein reactions in the Millon, xanthoproteic, tryptophane, and biuret tests.

Both contain 15 to 16% nitrogen and when examined by the Van Slyke method are shown to yield the eight forms of nitrogen distinguishable by this method (ammonia, melanine, arginine, lysine, cystine, histidine, and amino and nonamino nitrogen not precipitable by phosphotungstic acid) in proportions within the range of variation shown by such typical protein substances as casein, edestin, hair, and hemoglobin.

Both the pancreatic and the malt amylase preparations, when heated in solution, yield coagulated albumin and a proteose or peptone, the presence of the latter in the filtrate from the coagulum being shown by protein reactions and nitrogen content. The biuret reactions of these filtrates are pinker than those of the original enzyme solutions.

The malt amylase exerted its optimum diastatic (saccharogenic) power in a somewhat acid solution ($P_H^{+} 4.4 \pm 0.2$), whereas the optimum for the pancreatic amylase was slightly alkaline (P_H^{+} in the neighborhood of 8 to 8.5).

When each amylase is allowed to act upon soluble starch for thirty minutes at 40° under its optimum conditions of reaction and salt concentration, the pancreatic amylase shows a much higher activity than any yet obtained from malt. In such a test the pancreatic amylase forms about 10,000 times its weight of maltose, corresponding to a "new scale" diastatic power of 4,000 or a Lintner figure of about 6,000; the malt amylase forms about 4,000 times its weight of maltose giving a "new scale" diastatic power of 1570 or a Lintner figure of about 2350.

In long-digestion experiments at 40° the malt amylase has thus far been observed to form a total of 93,000 times its weight of maltose, whereas the pancreatic amylase has formed 1,200,000 times its weight of maltose.

The most highly purified preparations of pancreatic amylase show also a pronounced proteolytic action both upon casein and gelatin, while in the purified malt amylase preparations we have been unable to demonstrate any proteolytic activity.

In purified pancreatic amylase, the amylolytic and saccharogenic powers are concentrated in practically the same ratio; purified malt amylase of high saccharogenic activity does not show a correspondingly high amylolytic power, at least as measured by present methods.

In a solution of either amylase the activity deteriorates more rapidly the higher the temperature or the greater the dilution, but malt amylase

is always more stable than pancreatic amylase when simply standing in pure water solution.

On the other hand, pancreatic amylase is the more stable in 50% alcohol solution, and shows a more sustained activity in long-digestion experiments, in which there is present a relatively large amount of substrate together with such a concentration of "activating" electrolytes as had been found best adapted to each enzyme in the ordinary determination of diastatic power.

Both amylases deteriorate during dialysis, and much more rapidly at room temperature than at 5° to 10°. The increased deterioration in dialysis over simple standing in water at the same concentration is more readily demonstrable in the case of malt amylase.

The problem of the chemical nature of the enzymes is discussed in the light of the new observations on composition, coagulation, dialysis, activity, and deterioration.

We are greatly indebted to the Carnegie Institution of Washington for grants in aid of this investigation.

LABORATORY OF FOOD CHEMISTRY,
NEW YORK CITY.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK STATE COLLEGE
OF AGRICULTURE AT CORNELL UNIVERSITY.]

STUDIES ON THE ACTION OF EREPSIN.

BY FRANK E. RICE.

Received February 4, 1915.

Since the discovery of erepsin by Cohnheim,¹ in 1901, it has been investigated principally from the point of view of the physiologist. The properties of erepsin and the nature of its action as an enzyme, independent of any function it may have in the animal organism, have been less studied.

Erepsin is known to readily attack peptones and polypeptids, resolving them into their constituent amino acids. Only a few proteins have been found to be digested to any great extent, casein being the most notable example.

Maximum ereptic activity is manifested in weakly alkaline media. Vernon,² in studying the action of erepsin on Witte peptone, found that, while small quantities of alkali accelerated the digestion by erepsin, in higher concentrations it injured the enzyme to some extent. He concluded, that "over a certain range of alkalinity these two opposite influences nearly neutralize each other."

For ereptic experimentation, pure intestinal juice, or, a solution of

¹ *Z. physiol. Chem.*, **33**, 451-65 (1901); **35**, 134-140 (1902); **49**, 64-71 (1906); **51**, 415-24 (1907).

² *J. physiol.*, **30**, 330-70 (1903).

the enzyme prepared by extracting the macerated mucous coat of the small intestine with water or weakly alkaline solution, has been used. The latter preparations have been found to be more active.¹

No satisfactory method for standardizing the ereptic power of residues has ever been proposed. The activity of ereptic preparations has usually been only estimated by approximately determining the extent of digestion by them of polypeptids or peptones.

Experimental.

1. **Determination of Amino Nitrogen in Peptone Solutions.**—Witte peptone was found to be easily hydrolyzed by erepsin, and was used in all following experiments as substrate.

The hydrolysis of substances of peptone character is most accurately followed by determining the quantity of free amino nitrogen produced in the solution in the splitting up of the peptone molecules. Two methods for this determination have been principally used: the titration method proposed by Sørensen,² and the gasometric method of Van Slyke.³

The results obtained from these two methods have been compared by some investigators. White and Thomas⁴ preferred the Van Slyke method for their work. Abderhalden and Kramm,⁵ also Rogozinski,⁶ believed that the Sørensen method gave more reliable results.

Van Slyke pointed out that, among other things, the temperature of the reagents had an influence upon the apparent amount of nitrogen liberated in his apparatus. It seemed necessary to study the effect of temperature on the reaction in the apparatus, as well as the effect of time, which was shown by Abderhalden and Kramm to be considerable. The influence of the rate of shaking the apparatus was also determined.

The titration by the Sørensen method was carried out as suggested by the author. To 20 cc. of the peptone solution were added the neutralized formaldehyde-alcohol mixture and thymol phthalein; this was titrated with 0.2 *N* NaOH solution.

The Van Slyke apparatus was set up as described by the designer. It was connected with a motor, and during the reaction was shaken at the rate of about 250 vibrations per minute; the lower part of the mixing chamber passed through a distance of about three-fourths of an inch. Ten cc. portions of peptone were run each time, and 0.5 cc. amyl alcohol was added to prevent frothing.

¹ Hamburger and Hekma, *J. physiol. path. gén.*, 4, 805-19 (1902); Salaskin, *Z. physiol. Chem.*, 35, 419-25 (1902).

² *Biochem. Z.*, 7, 45-101 (1908).

³ *J. Biol. Chem.*, 9, 185-204 (1911); 12, 275-84 (1912).

⁴ *Ibid.*, 13, 111-16 (1912-13).

⁵ *Z. physiol. Chem.*, 77, 425-34 (1912).

⁶ *Ibid.*, 79, 398-414 (1912).

Experiment 1.—Witte peptone solution contained 3 g. per 120 cc. Result of the titration by the Sørensen method—4.28 mg. amino nitrogen per 10 cc.

Results obtained in the Van Slyke apparatus:

| | | | | | | |
|----------------------------|------|------|------|------|------|-----------|
| Temp. of reagents, | 22.5 | 22.5 | 24 | 24 | 28 | 28° |
| Time of reaction, | 6 | 8 | 6 | 8 | 6 | 8 minutes |
| Amino nitrogen per 10 cc., | 4.03 | 4.40 | 4.12 | 4.51 | 4.34 | 4.72 mg. |

Experiment 2.—In this experiment a peptone solution was used that had been digested with erepsin for some time. Titration by the Sørensen method gave 19.26 mg. amino nitrogen per 10 cc.

Results obtained by the Van Slyke method:

| | | | | | | | |
|-----------------------------|-------|-------|-------|-------|-------|-------|-----------|
| Temp. of room and reagents, | 15 | 15 | 15 | 23 | 23 | 27 | 27° |
| Time of reaction, | 7 | 9 | 11 | 5 | 7 | 5 | 7 minutes |
| Amino nitrogen per 10 cc., | 19.12 | 19.77 | 19.77 | 19.84 | 20.52 | 20.28 | 21.27 mg. |

Experiment 3.—To determine the effect of the rate of shaking the apparatus upon the quantity of gas evolved. The same peptone solution was used as in Experiment 2.

| | | | |
|----------------------------|-------|-------|-----------|
| Rate per minute, | 190 | 250 | 300 |
| Time, | 7 | 7 | 7 minutes |
| Temperature, | 23 | 23 | 23 |
| Amino nitrogen per 10 cc., | 14.41 | 20.52 | 21.20 mg. |

From these experiments it must be concluded that the Van Slyke method for the determination of amino nitrogen gives unreliable results unless extreme precaution is taken to keep all the conditions constant. The accuracy of results obtained by the formol-titration method of Sørensen is in no way affected by the method of manipulation; furthermore, it has been found that a number of determinations of amino nitrogen may be made more rapidly by the titration method than by the use of the Van Slyke apparatus. For these reasons, the Sørensen method for the determination of amino nitrogen has been used in the following experiments.

2. Preparation of the Erepsin-containing Material.—For the most part the procedure suggested by Cohnheim was followed. The mucous coat of the small intestine was ground in a mortar with sand, 0.1% sodium carbonate solution, and a little toluol, and finally allowed to stand at 38° for from one to ten days. This digest was made acid with acetic acid and filtered, whereby a clear, yellowish solution was obtained. To this was added saturated ammonium sulfate in the proportion of three parts to two of the enzyme solution. The residue, thus obtained, was removed by filtration and preserved in a desiccator over sulfuric acid.

In preparing a solution from this material, small quantities were shaken with 0.1% sodium carbonate solution, and dialyzed against flowing water for three to five days. (This length of time has always been found sufficient for the removal of ammonium salts.) This solution was used in digestion experiments with peptone. An aliquot portion was evaporated to dryness, and the loss on ignition of the solids determined. This weight has been taken as the quantity of enzyme present in the solution.

3. Action of Erepsin on Solutions Containing Varying Amounts of Peptone.—Peptone solutions of different concentrations were prepared, and allowed to be acted on by equal quantities of erepsin. In this, as well as in all succeeding erepsin digestion experiments, liberal use was made of toluol as preservative, and the digestion temperature was always 38° .

AMINO NITROGEN PER TEN CC.

| | | | |
|-------------------|------|------|----------|
| At beginning, | 3.08 | 4.07 | 5.14 mg. |
| End of ten hours, | 5.47 | 6.61 | 7.81 mg. |
| Increase, | 2.39 | 2.54 | 2.67 mg. |

It is seen that the amount of amino nitrogen split off from the peptone molecule by erepsin varies considerably with the initial concentration of the peptone solution. Therefore, in all following experiments care was taken that the digesting solutions were of the same concentration with reference to peptone. This was brought about in the following way: A peptone solution was prepared by boiling four or five grams of Witte peptone per 100 cc. of water, cooling, and filtering. Amino nitrogen was determined in the filtrate. For digestion experiments this peptone solution was diluted so that it finally contained 3.5 mg. amino nitrogen per 10 cc. A determination of total nitrogen by the Kjeldahl method shows such a solution to contain 33.46 mg. nitrogen per 10 cc.

4. The Digestion of Peptone by Erepsin as Affected by the Degree of Alkalinity.—In the following experiments the quantity of peptone in solution, also the quantity of erepsin, remained constant; the quantity of sodium hydroxide was varied. Digestions were run for ten hours.

Experiment 1.—

| | | | | | |
|--|------|------|------|------|------|
| CC. of 0.2 <i>N</i> NaOH per 60 cc., | 1 | 2 | 4 | 5 | 6 |
| Increase in mg. amino nitrogen per 10 cc., | 2.34 | 2.66 | 2.66 | 2.17 | 1.44 |

Experiment 2.—

| | | | | | |
|--|------|------|------|------|------|
| Cc. of 0.2 <i>N</i> NaOH per 60 cc., | 1.7 | 2.0 | 2.5 | 3.0 | 3.5 |
| Increase in mg. amino nitrogen per 10 cc., | 1.85 | 1.85 | 1.83 | 1.85 | 1.80 |

There seems to be no definite point which would be considered optimum for ereptic action. The addition of 1.7 to 4 cc. of 0.2 *N* NaOH per 60 cc. of the digesting solution accelerates the digestive action to about the same extent; and, the activity is seen to be diminished where alkali is added in greater or less quantities.

In all succeeding experiments, digesting solutions contain 2 cc. 0.2 *N* NaOH per 60 cc.

5. Action of Alkali on Peptone.—Vernon found that sodium carbonate had a slight hydrolytic action on peptone as measured by the biuret method. In the following experiment a solution of peptone was prepared of the same strength used in the erepsin determinations; each 60 cc. contained 2 cc. of 0.2 *N* NaOH. The solution was preserved with toluol, and allowed to stand at 38° . At intervals, portions of the solution were

titrated by the formol-titration method and the amount of aminonitrogen calculated.

| | | | | | |
|----------------------------|------|------|------|------|----------|
| Time, | 0 | 1 | 4 | 10 | 34 days. |
| Amino nitrogen per 10 cc., | 3.50 | 3.53 | 3.53 | 3.53 | 3.50 mg. |

There is no hydrolysis of peptone by alkali of the strength used in erepsin digestions.

6. Course of the Digestive Action of Erepsin on Peptone with Regard to Time.—In this experiment the amounts of peptone and sodium hydroxide in the solutions are constant, and the amount of erepsin is varied: A, 3.81 mg.; B, 7.62 mg.; C, 13.33 mg. per 60 cc. of solution. Results are expressed in mg. amino nitrogen per 60 cc.

| | | | | | | | | |
|---------|-------|-------|-------|-------|-------|-------|-------|----------|
| Time, 0 | 4 | 7 | 10 | 13 | 24 | 52 | 144 | 840 hrs. |
| A, | 21.18 | 25.68 | 28.62 | 32.76 | 33.84 | 42.66 | 54.26 | 89.46 |
| B, | 21.18 | 28.92 | 34.02 | 40.80 | 43.50 | 56.34 | 75.26 | 113.56 |
| C, | 21.84 | 34.80 | 42.18 | 50.82 | 55.68 | 72.43 | 93.32 | 135.24 |

By plotting the quantity of amino nitrogen in solution with time (see Fig. 1), it is seen that the "curves" are nearly straight until after ten

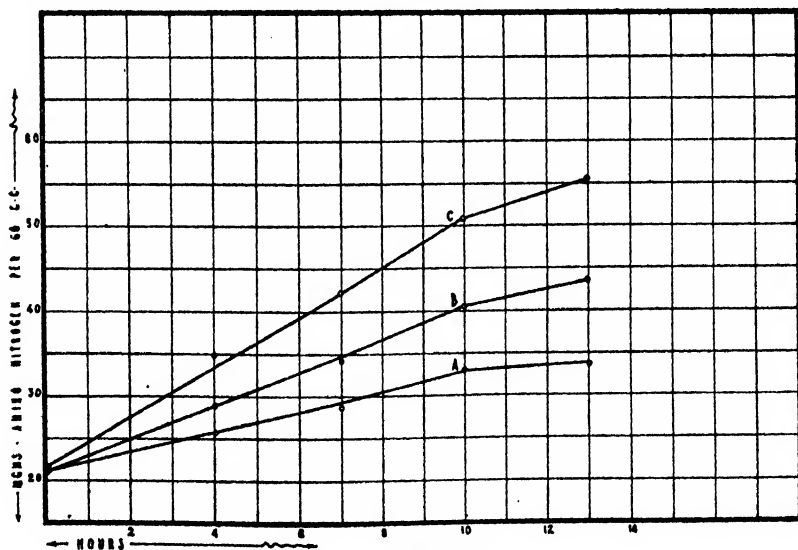


FIG. 1.

hours, *i. e.*, the quantity of amino nitrogen split off by the enzyme is nearly proportional to the time, at the beginning of the reaction. After ten hours, however, there is less and less hydrolysis per unit of time and the curves approach one another (Fig. 2). This latter phenomenon was also pointed out by Bayliss in the action of trypsin on caseinogen.¹

Since hydrolysis seemed to proceed at a uniform rate during the first

¹ Bayliss, "The Nature of Enzyme Action."

ten hours, digestions were run for this length of time in the following experiments where comparative results were required.

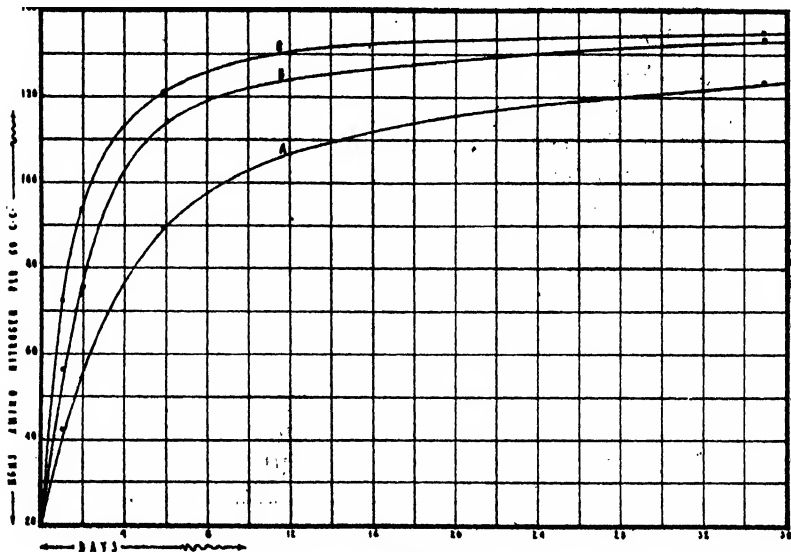


FIG. 2.

7. Digestion with Varying Amounts of Erepsin.—All solutions were prepared as follows: Enough strong peptone solution was measured out to contain 21 mg. of amino nitrogen. To this was added 2 cc. 0.2 *N* NaOH, the erepsin solution, enough water to make 60 cc., and about 8 drops of toluol. Digestions were allowed to proceed for ten hours at 38°. At the beginning and end of the ten hour period, 20 cc. portions were titrated, and the quantity of amino nitrogen calculated in mg. per 60 cc.

| | | | | | | | |
|------------------------------|------|-------|-------|-------|-------|-------|-------|
| Mg. erepsin per 60 cc., | 1.25 | 2.50 | 5.00 | 7.50 | 10.00 | 15.00 | 20.00 |
| Mg. amino nitrogen produced, | 6.00 | 10.08 | 16.80 | 22.68 | 28.20 | 37.02 | 44.68 |

In the study of the action of erepsin on deuterioalbumose, Kutscher and Seeman¹ found the amount digested to be proportional to the square root of the concentration of the erepsin. This may be represented by the formula

$$N/E^{1/2} = \text{constant},$$

where *N* is the amount of hydrolysis produced by *E*, the amount of erepsin.

If, however, the amount of hydrolysis is proportional to the amount of active enzyme, as has been found in the case of some enzymes, the following formula should hold:

$$N/E = \text{constant}$$

In the following table the above figures have been applied to these

¹ *Z. physiol. Chem.*, 35, 432-58 (1902).

formulae: (N and E are taken in mg. amino nitrogen and erepsin per 60 cc., respectively).

| | | | | | | | |
|----------------------------------|------|-------|-------|-------|-------|-------|-------|
| E, | 1.25 | 2.50 | 5.00 | 7.50 | 10.00 | 15.00 | 20.00 |
| N, | 6.00 | 10.08 | 16.80 | 22.68 | 28.20 | 37.02 | 44.88 |
| N/E \times 100: | 480 | 403 | 336 | 302 | 282 | 247 | 224 |
| N/E ^{1/4} \times 100: | 537 | 637 | 752 | 828 | 891 | 955 | 1003 |

This would indicate that neither the direct proportion nor the square root law hold; but the ratio which would most nearly yield a constant should be found between the two.

The ratio, which has been found to apply for nearly all erepsin preparations studied, is $-N/E^{1/4} = \text{constant}$. In the following table the above results are applied to this formula:

| | | | | | | | |
|----------------------------------|------|-------|-------|-------|-------|-------|-------|
| E, | 1.25 | 2.50 | 5.00 | 7.50 | 10.00 | 15.00 | 20.00 |
| N, | 6.00 | 10.08 | 16.80 | 22.68 | 28.20 | 37.02 | 44.88 |
| N/E ^{1/4} \times 100: | 508 | 507 | 502 | 500 | 501 | 485 | 474 |

This rule is seen to hold quite well within the limits of experimental error, where the extent of hydrolysis is not too great. In the last two solutions the reaction proceeded so rapidly that the accumulating products have checked the action of the enzyme.

In a similar manner the results obtained on page 323 may be used:

| | | | |
|----------------------------------|-------|-------|-------|
| E, | 3.81 | 7.62 | 13.33 |
| N, | 11.58 | 19.62 | 28.98 |
| N/E ^{1/4} \times 100: | 425 | 428 | 416 |

Still another preparation gave similar results:

| | | | | |
|----------------------------------|------|-------|-------|-------|
| E, | 5 | 10 | 15 | 20 |
| N, | 9.12 | 15.96 | 21.12 | 26.58 |
| N/E ^{1/4} \times 100: | 273 | 284 | 277 | 281 |

In all the above cases the erepsin was obtained from the dog. The following results were obtained on erepsin extracted from the horse intestine:

| | | | | |
|----------------------------------|------|------|-------|-------|
| E, | 9.8 | 14.7 | 19.6 | 29.4 |
| N, | 6.90 | 9.60 | 11.82 | 17.10 |
| N/E ^{1/4} \times 100: | 125 | 128 | 127 | 135 |

In the following table numbers I and II show the rule to apply to the action of erepsin obtained from the rabbit, erepsin from the cat (III) shows similar results. The figures under IV were obtained for a solution of erepsin from a dog, which had stood at about 12° for one year.

| | III. Cat. | | | | IV. Dog. | | | |
|-------------------------------------|-----------|-------|-------|-------|----------|-------|-------|-------|
| E..... | 9.8 | 9.96 | 11.8 | 23.6 | 4.5 | 9.0 | 4.2 | 8.4 |
| N..... | 19.6 | 16.68 | 9.42 | 15.48 | 4.13 | 6.47 | 7.14 | 12.24 |
| N/E ^{1/4} \times 100.... | 180.0 | 179.0 | 148.0 | 145.0 | 133.0 | 125.0 | 243.0 | 248.0 |

It is not claimed that erepsin will act according to this law on all substrates and under all conditions, but under the peculiar conditions of these

experiments the law has been found to hold well within the limits of experimental error.

8. A Method for Comparing Ereptic Power of Extracts.—As has already been pointed out, if a solution of Witte peptone of such strength that there is present 21 mg. amino nitrogen per 60 cc., containing also 2 cc. 0.2 *N* NaOH, be acted upon by erepsin for ten hours, the amino nitrogen liberated will be proportional to the weight of erepsin raised to the three-fourths power, provided, further, that there is not greater enzyme activity than which would liberate more than 30 mg. of amino nitrogen per 60 cc. In other words, $N/E^{3/4}$ is constant under the conditions stated, where *N* = the amount of amino nitrogen produced, and *E* = weight of erepsin extract.

In the following experiments where activity of erepsin preparations was to be compared, the constant— $N/E^{3/4} \times 100$ —was determined for each; quantities *N* and *E* were taken in milligrams. This value was designated as *ereptic power*.

9. Purification of Enzyme Extracts.—Very few attempts have been made to prepare erepsin in any state of purity. Cohnheim tried several methods of purification but was unable to get a preparation free from protein. Euler¹ and Raubitschek² used special methods for preparing erepsin solutions from the mucous coat, but have not compared the power of these preparations with those obtained by the simpler methods first suggested by Cohnheim.

Cohnheim used an alkaline physiological salt solution for extracting the enzyme from the mucous coat. Erepsin-containing residues were precipitated from these solutions by the addition of saturated ammonium sulfate in the proportion of three parts to two of the enzyme solutions. Some experiments were made to determine the effect of carrying out these details upon the ereptic power of the preparations finally obtained.

Experiment 1.—Equal portions of the mucous coat were digested with equal quantities of the following: A, 0.1% sodium carbonate solution; B, water; C, 0.1% acetic acid solution. Erepsin extracts were obtained from these with ereptic power as follows:—A 144, B 144, C 88.

The use of 0.1% sodium carbonate solution containing 0.9% sodium chloride, and of a solution of 0.1% sodium carbonate alone, was tested similarly. The former solution yielded an extract with ereptic power, 215, and the latter, 248.

It seems that there is no advantage in digesting the mucous coat with alkaline solution, nor in using an alkaline solution containing sodium chloride, over digesting with pure water. Digestion with weak acid seems to injure the enzyme slightly.

Experiment 2.—In this experiment three extracts were prepared: A.—After the digestion of the mucous coat with 0.1% sodium carbonate solution, the mixture was

¹ *Z. physiol. Chem.*, 51, 213-25 (1907).

² *Z. exp. Path. Ther.*, 4, 674-80 (1907).

acidified and filtered, and a portion was dialyzed for ten days. (This length of time was found necessary for the removal of substances titratable by the formol-titration method.) B.—To a portion of the filtrate obtained in A, ammonium sulfate was added to one-third saturation. This was filtered, the residue discarded, and to the filtrate ammonium sulfate added to two-thirds saturation. Upon again filtering the residue was suspended in 0.1% sodium carbonate, dialyzed, and filtered. C.—To a portion of the filtrate obtained in A, ammonium sulfate was added to two-thirds saturation at once, and the residue treated as in B. The ereptic power of the enzyme in solution A was found to be 153, solution B 180, solution C 180.

These results indicate that there is no advantage in fractional precipitation with ammonium sulfate, and that only slightly more active residues may be obtained by the use of ammonium sulfate at all. In another experiment the erepsin in the original solution after dialysing was even more active than that obtained by precipitating with ammonium sulfate.

Other conditions being identical, it has been found that the longer the time of contact of the macerated mucous coat with the solvent, the more powerful the erepsin preparations obtained. Mucous coat from a cat was divided into two portions and each digested with 0.1% sodium carbonate solution: (1) for five days, (2) for ten days. The ereptic power of the preparation finally obtained from (1) was found to be 175, and that from (2), 240. It has usually been found that very little is gained by extracting the mucous coat more than ten days.

Sørensen¹ obtained erepsin solutions by pressing the juice from the mucous coat by means of the Büchner press.

In two cases, pressed juice was obtained from portions of the mucous coat by means of the Büchner method.² These solutions were precipitated by saturated ammonium sulfate solution. Residues thus obtained exhibited much less ereptic power than those obtained by the solution method. Furthermore, by extracting the cake remaining behind in the press, with 0.1% sodium carbonate, it was found that the greatest part of the erepsin had been adsorbed, and that this portion was more active than that which was pressed out.

Other methods that were tried for preparing more active erepsins, *i. e.*, preparations with less admixture of impurities, included the Jacoby uranyl phosphate method,³ precipitation of the enzyme or its impurities along with cholesterol,⁴ precipitation with alcohol, and extracting the erepsin-containing precipitates with organic solvents. In none of these instances was there obtained a preparation of greater ereptic activity than that resulting from the direct solution of the mucous coat and dialyzing.

¹ *Biochem. Z.*, 7, 45-101 (1908).

² Abderhalden, *Handbuch der chemischen Arbeitsmethoden*, 3, 394.

³ *Z. physiol. Chem.*, 30, 135-48 (1900).

⁴ Schrumpt, *Beitr. chem. Physiol. u. Path.*, 6, 396-97 (1905).

Adsorbents were found useful by Michaelis¹ in separating invertin from its protein admixture. The following experiment exhibits the behavior of erepsin in contact with kaolin and hydrated aluminum oxide.

To each of three equal quantities of erepsin solution was added 1 g. of kaolin. One (A) was made slightly acid with hydrochloric acid; a second (B) was made alkaline with sodium hydroxide; the third (C) remained neutral. All were made up to the same volume, shaken five minutes, and filtered. Ereptic activity of the filtrates was determined with the following results:

| | | | |
|----------------|----------|----------|----------|
| E | (A), 5.7 | (B) 17.3 | (C) 10.2 |
| N, | 0 | 14.03 | 10.07 |
| Ereptic power, | 0 | 165 | 176 |

The original solution had an ereptic power of 160. Kaolin in neutral or alkaline solution seems to remove more impurity than enzyme, however, the increase in ereptic activity produced by this treatment is not of such magnitude that it may be considered very important in preparing more powerful residues.

A suspension of hydrated aluminum oxide was prepared by adding ammonium hydroxide to a solution of aluminum acetate, and washing the precipitate by decantation several times. In a manner similar to that described above, the action of this on erepsin in acid, alkaline, and neutral solution was tested. It was found in all three cases that the enzyme was completely adsorbed from its solution by the hydrated aluminum oxide.

The results obtained in this experiment are of interest principally in the consideration of erepsin as a colloid.

10. Action of Erepsin on Blood Fibrin.—Certain investigators have found blood fibrin to be slightly digested by erepsin, others have concluded that there was no action. Cohnheim believed that fibrin was not attacked. Kutscher and Seeman found slight action. Vernon believed that erepsin had little or no action. Weinland² found that fibrin was slightly digested by extracts made from the intestinal mucous coats of the pig, however, he believed this to be due to the presence of trypsin which he was unable to wash from the intestines with which he worked.

In the following experiment the action of erepsin on dried blood fibrin was tested. Portions were added to erepsin solutions, some sodium hydroxide solution added, and the whole made up to 50 cc. In all cases toluol was added as preservative. Digestion was allowed to proceed at 38°. At the end of the digestion periods, the solutions were filtered, brought to the neutral point using neutral red as indicator, and the amino nitrogen in solution determined by the titration method of Sørensen.

¹ *Biochem. Z.*, 7, 488-92 (1908).

² *Z. Biol.*, 45, 292-97 (1903).

Experiment 1. Effect of varying the degree alkalinity.—In each case there was present 1 g. of fibrin, and 33 mg. of erepsin per 50 cc. To A was added 0.25 cc. 0.2 *N* NaOH, to B 1.5 cc. In the blank (C) was used 1.5 cc. 0.2 *N* NaOH, but no enzyme. The digestion ran three days. Upon determining the quantities of amino nitrogen in the filtrates, the following results were obtained: A 2.8 mg. per 10 cc., B 0.42 mg., C 0.28 mg.

It is seen that in a very weakly alkaline solution, erepsin attacked commercial fibrin quite vigorously, however, where 1.5 cc. 0.2 *N* NaOH was added, the quantity of amino nitrogen split off was very little greater than that in the blank. It has been found that the action of trypsin upon fibrin is very little hindered by the presence of NaOH in the higher concentration. Equal quantities of trypsin acting upon one gram of fibrin for three days produced 4.62 mg. of amino nitrogen per 10 cc. of filtrate when 0.25 cc. 0.2 *N* NaOH was present in 50 cc., and 4.20 mg. when 1.5 cc. was present. These facts can be made use of in testing erepsin preparations for presence of trypsin. In the following case this is illustrated:

A solution containing 23 mg. of erepsin (from horse), and 1.5 cc. 0.2 *N* NaOH was made up to 50 cc., and 1 g. fibrin added (A). Another solution (B) was prepared similarly, 5 mg. trypsin being added instead of erepsin. A third preparation (C) contained 23 mg. of the same erepsin, 5 mg. trypsin, and the same quantity of sodium hydroxide. The blank (D) contained only sodium hydroxide and fibrin. Digestion was run three days. Filtrate from A was found to contain 0.63 mg. amino nitrogen per 10 cc.; B, 1.74, C, 2.17 mg.; D, 0.56 mg.

Experiment 2. Action of Erepsin on Fresh Blood Fibrin.—A quantity of fibrin was obtained by whipping fresh horse blood. This was washed, first in flowing water to remove the main part of the blood, then, ground in a mortar to break up the large clumps, and again washed many times by decantation with hot water and 10% sodium chloride solution—finally with hot water to remove all sodium chloride. The action of erepsin and trypsin on this material was tested in a way similar to that described above. In all tests there were approximately equal amounts of fibrin.

(A) contained erepsin and 0.25 cc. 0.2 *N* NaOH. (B) contained an equal quantity of erepsin and 1.5 cc. 0.2 *N* NaOH. In (C) and (D) were equal quantities of trypsin, also 0.25 cc. and 1.5 cc. 0.2 *N* NaOH, respectively. (E) was run as a blank—1.5 cc. 0.2 *N* NaOH, but no enzyme. All solutions were made up to 50 cc. Digestions were run for three days. In the filtrate from (A) was found 1.4 mg. amino nitrogen per 10 cc.; (B), 0.21; (C), 2.17; (D), 2.31; (E), 0.

This shows that erepsin has considerable action of fresh blood fibrin, also; and it is seen again that the higher concentration of alkali almost completely checks the action of erepsin but does not hinder the digestive action of trypsin on fibrin.

11. Action of Erepsin on Gelatin.—Hamburger and Hekma,¹ using the intestinal juice of man, found no action on gelatine.

A solution of gelatin was prepared by dissolving five grams in 200 cc. of hot water, and adding 8 cc. of 0.2 *N* NaOH. Digestions were made as follows:

¹ *J. physiol. Path. gén.*, 4, 805-19 (1902).

(1) To 60 cc. of gelatin solution were added 15 cc. (containing 17 mg.) of erepsin; (2) to 60 cc. of gelatin solution were added 15 cc. (containing 15 mg.) of trypsin; (3) was run as blank—60 cc. gelatin solution plus 15 cc. water. Amino nitrogen, as determined by the formol-titration method, was per 10 cc.

| | (1). | (2). | (3). |
|--------------------------|------|------|------|
| At beginning..... | 0.74 | 1.09 | 0.67 |
| End of twenty hours..... | 3.29 | 2.94 | 0.67 |
| End of two days..... | 4.86 | 3.18 | 0.65 |

The erepsin used in the above experiment was obtained from a rabbit, and it was found by testing its action on fibrin to be free from trypsin. The experiment shows the action on gelatin to be very great, certainly no less than that produced by an equivalent amount of trypsin.

12. Erepsin as an Autolytic Enzyme.—Kutscher and Seeman found that if the mucous coat of the small intestine be allowed to stand under toluol or chloroform, autodigestion takes place.

Some observations were made to determine whether or not autodigestion of the mucous coat of the small intestine was in any way related to the presence of erepsin. The ground mucous coat was allowed to stand under water, or weak solutions of acid, or alkali, with toluol as preservative. All solutions were made acid and filtered. Portions of the filtrates were neutralized, using neutral red as indicator, and the amino nitrogen determined by the formol-titration method. The quantity of amino nitrogen was taken as a measure of the extent of autolysis.

In this experiment the intestinal mucous coat of the cat was divided into three portions, and digested for five days at 38° with the following solutions: (1) 0.1% sodium carbonate, (2) water, (3) 0.1% acetic acid. Determination of amino nitrogen in the filtrates gave the following results: (1) 11.2 mg. amino nitrogen per 10 cc., (2) 9.5 mg., (3) 6.8 mg.

If autolysis can be measured by the amount of amino nitrogen produced, these results show that in this case it takes place to the greatest extent in alkaline solution, whereas, in most tissues this process has been found to be most active in acid media.

It has been found that in cases where autolysis of the tissue had been most active, more powerful erepsin preparations could be obtained. The following example illustrates this:

The intestinal mucous coats of two dogs were extracted with approximately equivalent quantities of 0.1% sodium carbonate solution. Filtrate from (A) was found to contain 10.8 mg. amino nitrogen per 10 cc., from (B) 35.9 mg. Ereptic power of the preparation obtained from solution (A) was 200, from solution (B) 440.

These results, together with the fact already mentioned—that somewhat more powerful preparations could be obtained by allowing the initial extraction of the mucous coat to continue for a longer period of time, would lead to the conclusion that autolysis of the mucous coat tissue is related to the activity of the erepsin.

In the following experiment the intestinal mucous coat of a cat was

divided into two portions. From one part, erepsin was prepared in the usual way. This preparation was believed to be free from other enzymes. The fibrin test for trypsin was negative; also, the constant, $N/E^{1/4}$ was found to hold when testing its action on peptone. The remainder of the mucous coat was heated to destroy enzymes present. This was thrown on cheese cloth and carefully washed with water. Only the larger portions of the tissue were then used:

(1) To a part of the mucous coat was added the erepsin, 0.5 cc. 0.2 *N* NaOH and water to make 30 cc.; (2) this was run as blank and contained 0.5 cc. 0.2 *N* NaOH and water only. These preparations were digested ten days at 38°, then filtered. Filtrate from (1) was found to contain 3.4 mg. amino nitrogen per 10 cc., (2) 0.4 mg.

While these results seem to show that erepsin may be the cause of autolysis in the tissue of the mucous coat of the small intestine, it is not proved, however, that, in addition, other autolytic enzymes are not present in the fresh tissue.

13. Permanence of the Enzyme.—The ereptic preparations have generally been preserved in one of two ways: (1) the residue obtained from the precipitation of ammonium sulfate, kept in a desiccator over sulfuric acid; (2) a solution in water that has been dialysed and is neutral, and kept at a temperature of 10° to 15°.

A preparation obtained from the horse, and preserved according to the former method, had an ereptic power at the beginning of 109; at the end of eleven days, 105; thirty-five days, 102; sixty days, 97. Dog erepsin residues gave the following results: ereptic power of the fresh residue, 278; the same, fifty days old, 232. Another preparation from the dog showed an ereptic power of 119 when fresh, but after ten months it had fallen to 58.

Some results on the loss in activity of the dialysed aqueous solution are as follows: A solution containing dog erepsin had, when fresh, ereptic power of 277, at the end of ten days, 262. Fresh solution containing horse erepsin exhibited a power of 100; at the end of ten days, 86.

The following results on two dog erepsin preparations show the change on standing in aqueous solutions for longer periods: Fresh solution, ereptic power, 338 and 425; 8 months old, 248 and 254; 12 months old, 222 and 245.

Vernon recommended dilute alcohol as a preservative for erepsin. However, Cohnheim believed that treatment with alcohol weakened the enzyme. In this experiment a solution of dog erepsin with ereptic power of 320 was divided into two portions and treated as follows: to (1) was added one-half volume of alcohol, and to (2) was added the same quantity of water. At the end of six months the ereptic power of (1) was 196, and of (2) 220. These results show that weak alcohol does have an injurious action on erepsin, and that it is better to preserve the enzyme in water.

14. Effect of Bacterial Growth in Erepsin-containing Solutions.—

In a number of cases where the preservative was allowed to disappear from erepsin preparations, or, where the preservative was added in insufficient amounts, very marked bacterial decomposition took place. This was accompanied by the appearance of a tryptic enzyme in the solutions. Accordingly, such solutions became useless for ereptic experimentation; they exhibited strong action on fibrin and the three-fourths law was found to no longer hold.

A portion of a solution which had become contaminated, acting on 1 g. of fibrin for two days, produced 7 mg. soluble amino nitrogen per 10 cc., when there was present 1.5 cc. 0.2 *N* NaOH. The same solution gave the following results when tested on peptone:

| | | | | |
|--------------------------|-------|-------|-------|-------|
| E, | 20 | 30 | 40 | 50 |
| N, | 11.10 | 14.10 | 16.38 | 18.30 |
| $N/E^{3/4} \times 100$: | 117 | 110 | 103 | 97 |

Some of the ammonium sulfate residues became decomposed, and showed similar results. Likewise, in some cases where the intestine was not used for a number of days after the death of the animal, enzyme preparations obtained, gave results of a similar order. It is therefore necessary to guard against bacterial growth in the preparation of enzyme solution by the liberal use of toluol. Many times thymol may be added to advantage in addition to toluol.

Summary and Conclusions.

Witte peptone is quite readily hydrolyzed by erepsin. The extent of hydrolysis may be measured by determining the quantity of free amino nitrogen split off from the peptone molecules. The Sørensen formol-titration method was found more satisfactory than the Van Slyke method for the determination of free amino nitrogen in peptone solutions.

The quantity of amino nitrogen split off by the action of erepsin on peptone varies with the amount of peptone in solution.

The extent of hydrolysis of peptone produced by moderate amounts of erepsin during the first ten hours is directly proportional to the time.

The quantity of amino nitrogen split off during the first ten hours is proportional to the weight of erepsin raised to the three-fourths power. This was found true for preparations obtained from the dog, cat, rabbit, and horse.

Most active erepsin preparations may be obtained as follows: The small intestine, obtained as soon as possible after the death of the animal, is split open, and washed well with running water. The mucous coat is scraped away with a piece of glass. This is ground with sand and a little water in a mortar, transferred to a 0.1% sodium carbonate solution, and allowed to stand with frequent shaking at 38° for ten days. A preservative must be present. The suspension is then filtered through cheese

cloth, and the filtrate made slightly acid with acetic acid. Upon allowing to stand in a warm place for a short time the suspended matter flocculates, and may be rapidly filtered off, using an ordinary filter. The filtrate is dialysed against flowing water for ten days. A nearly colorless solution is thus obtained, which responds to the biuret test very weakly; it contains only a trace of amino nitrogen. It exhibits ereptic action quite strongly.

Erepsin is completely adsorbed from acid, alkaline, and neutral solutions by aluminum hydroxide; it is also adsorbed by kaolin in acid solution. It is not in the least adsorbed by kaolin from neutral or alkaline solution.

Erepsin attacks fibrin in very weakly alkaline solution. Upon slightly increasing the amount of alkali in solution (1.5 cc. 0.2 *N* NaOH per 50 cc.) there is practically no action. While ereptic action on fibrin is held in check by this strength of alkali, tryptic digestion is scarcely hindered. This fact may be made use of in testing erepsin preparations for the presence of trypsin.

Erepsin hydrolyses gelatin very rapidly.

Experiments indicate that erepsin attacks the tissue of the mucous coat of the small intestine, from which it may be concluded that it is the enzyme, or one of the enzymes, inducing autolysis of that tissue. Autolysis in this case is greatest in alkaline solution.

The residues obtained by precipitation with ammonium sulfate and preserved dry, seem to lose in ereptic power somewhat more rapidly after the first few days than neutral aqueous solutions. Dilute alcohol is a less satisfactory medium for preserving erepsin than water.

Bacterial growth should be prevented in all stages of the preparation of erepsin, since it may be accompanied by the production of proteolytic enzymes.

The writer wishes to express his thanks to Professor Andrew Hunter at whose suggestion this work was begun, and who took an active interest in its progress. Professor M. Dresbach and Mr. A. F. Livingston of the Cornell Medical College kindly provided most of the animal intestines used.

ITHACA, N. Y.

ON THE PHYSIOLOGICAL ACTIVITY OF COMBINED HYDROCHLORIC ACID.¹

By J. H. LONG.

Received March 26, 1915.

The question of the efficiency of hydrochloric acid, when combined with different compounds in the digestion of proteins by pepsin, has

¹ This investigation has been made with the assistance of a grant from the Committee on Therapeutic Research, Council on Pharmacy and Chemistry, American Medical Association.

received much attention in earlier years but has been settled only in a very general way. The acid combined with inorganic bases is of course inactive in this direction, but as to the behavior of proteins or protein derivatives in combination there was, and there is yet, some dispute.

The early discussions of the question we find between 1880 and 1890, when, by the introduction of new indicators, the conception of acid held by protein could be more easily followed. Slightly earlier than this Hoppe-Seyler had made the observation that hydrochloric acid gradually combines with the products of peptic digestion and that the rapidity of digestion diminishes because of this combination.¹ Danilewski, in 1880,² discusses the nature of this acid combination and refers the property to the gradual formation, or liberation, of bodies of amine character. With the progress of digestion the amounts of these would increase. To follow the changes in the amount of free acid or free alkali after treatment of protein with an excess of either, he recommends the use of tropaeolin oo and ooo. His observations were somewhat inexact, however.

The use of phloroglucin and vanillin mixture as an indicator for "free" acid was introduced by Guenzburg in 1887,³ and the sugar and resorcinol mixture by Boas a little later.⁴ Congo red seems to have been recommended for physiological investigations somewhat earlier. Through the aid of these indicators it became possible to study much more conveniently the behavior of hydrochloric acid in artificial digestion processes, as well as in the stomach. The distinction between the behavior of phenolphthalein and methyl orange in the titration of digestion mixtures was gradually cleared up.

It was shown by v. Pfungen⁵ and others that the hydrochloric acid which combines with protein is so loosely held that it may be dissociated more or less readily by dilution with water, although there is no separation by dialysis. For this reason the proposed method for the recognition of free hydrochloric acid by the addition of cinchonine and extraction with chloroform must be of no value in the separation of actually free hydrochloric acid in excess over the protein. However, the differences in behavior between the more complex proteins and their derivatives or digestion products was not at this time recognized.

An important addition to the methods for the identification of actually "free" acid was made by F. A. Hoffmann⁶ when he proposed to employ the speed of the inversion of cane sugar as a measure of acidity present

¹ "Physiologische Chemie," p. 231.

² *Maly's Jahresber.*, 10, 5 (1880); *Liebig and Kopp's Jahresber.*, 1880, p. 1033.

³ *Centralbl. klin. Med.*, 9, 185 (1887).

⁴ *Ibid.*, 9, 817 (1887).

⁵ *Maly's Jahresber.*, 19, 240 (1889).

⁶ *Centralbl. klin. Med.*, 10, 793; 11, 521; *Maly's Jahresber.*, 19, 256 (1889); 20, 234 (1890).

in such cases where protein is concerned. The method had been used successfully in other mixtures. In these papers the notion of mass action in the combination of acid and protein is brought out sharply, as well as the disturbance through dissociation by water. Substances like peptone hydrochloride and betain hydrochloride dissociate in water and permit the acid to act as physiologically free. But substances like quinine hydrochloride, on the other hand, hold the acid in such combination that it is not available for peptic digestion. The distinction is brought out by E. Salkowski and M. Kumagawa,¹ who were able to show that hydrochloric acid combined with leucine or other amino acid so as to form a chemically neutral salt is still physiologically active, since in aqueous solution the acid leaves the leucine and promotes peptic digestion.

In a later publication, following criticism of this point of view by Rosenheim² and Hoffmann,³ Salkowski⁴ goes more fully into the subject and shows the conditions under which the hydrochloric acid may become inactive. This follows when a very large amount of egg albumin or fibrin is digested with a limited amount of the leucine hydrochloride or similar substance. It might have been pointed out that digestion with ordinary free acid would be very slow, or might even fail, under the same conditions. This last view is a contradiction of the one advanced by Schiele,⁵ according to which the only active acid is that which is already in combination with protein. The so-called free acid would be useful only in combining with the digestion products formed beyond the albumose stage. As these products of hydrolysis are formed, more and more acid will be taken up. Any excess of acid beyond this may be harmful, or at any rate unnecessary.

The rather numerous investigations which have appeared on the question of the behavior of combined hydrochloric acid leave a number of points still undecided. The real activity of the acid in presence of an excess of protein calls for a fuller study, and especially by aid of the electrometric methods which permit a determination of true acidity without the introduction of anything to disturb existing conditions of equilibrium. In the work to be described below, the digestive activity of hydrochloric acid combined with certain amino acids, on the one hand, and with complex proteins, on the other, is compared. As the experiments in this investigation are practically all comparative, digestion is measured by the simple means of filtration and Kjeldahl determinations of the soluble nitrogen. For the purpose this affords a satisfactory measure of what may be called "digestion."

¹ *Virchow's Archiv.*, 122, 235 (1890).

² *Maly's Jahresber.*, 21, 221 and 222 (1891).

³ *Ibid.*, 21, 204 (1891).

⁴ *Virchow's Archiv.*, 127, 521 (1892).

⁵ *Maly's Jahresber.*, 25, 272 (1895).

I. The Behavior of Betain Hydrochloride.

This substance was chosen to illustrate the behavior of an amino acid-like body, because of its comparatively simple structure, and the ease with which it may be obtained in pure condition. It may be secured from chemical dealers and at the present time is obtainable, also, in nearly pure form under the name of *acidol* from one of the large German chemical companies. The original source is the residue from beet-sugar manufacture. The free hydrate has been given the formula $(\text{CH}_3)_3 \equiv \text{N} \cdot \text{OH} - \text{CH}_2\text{COOH}$, while the hydrochloride is $\text{Cl}(\text{CH}_3)_3 \equiv \text{N} - \text{CH}_2\text{COOH}$. For the experiments below the commercial product was crystallized from hot alcohol. The purified salt, on titration with 0.1 N alkali and phenolphthalein, gave a sharp result for the halogen acid present. The end point in the titration with methyl orange is nearly as sharp, but the volume of alkali added is slightly less. In other words, the basic behavior comes slightly in evidence here. The titration with alkali and phenolphthalein is complete. What is the actual [H] ion concentration in solutions of this salt? To determine this a series of solutions were made to contain definite amounts of HCl. These solutions were used in digestion experiments to be given. The hydrochloride used, as crystallized above, had a purity of 98.2%, shown by silver and alkali titrations.

In preliminary experiments on the rapidity of digestion by aid of pepsin I used in one instance 5 g. of fibrin with 4.42% of nitrogen, 50 mg. of pepsin, 500 mg. of the hydrochloride and 50 cc. of water. The mixture was digested at 40°. In two hours the reaction was far advanced, with most of the fibrin in solution, but it was continued fourteen hours longer, sixteen hours in all. The mixture was boiled and filtered, the residue being well washed. In the filtrate the soluble nitrogen was found to be 231.7 mg., as the mean of two experiments. This is greater than the total nitrogen of the fibrin, but must be diminished by the nitrogen of the betain hydrochloride and the pepsin, 45.5 mg. $231.7 - 45.5 = 186.2$. As the total fibrin nitrogen was 221 mg. the result shows a digestion value of 84.2%.

In a similar experiment with eggs I employed the coagulum from 1.2 g. of egg albumin powder containing 70% of dry protein. In the mean of two experiments the nitrogen found was 131.6 mg. This must be diminished by the nitrogen of a blank experiment in which killed pepsin was used. At the end of each digestion the mixtures were exactly neutralized with sodium hydroxide, boiled and filtered. In this way the neutralization precipitate was excluded. $131.6 - 44.1 = 87.5$ mg. of nitrogen from the more advanced digestion, which was practically completed in two hours, but which was continued over night as above.

These experiments indicate an advanced degree of digestion, and

nearly as much as would have been obtained by the use of the equivalent amount of free hydrochloric acid.

For most of the experiments detailed below a solution was used which contained 10.69 g. of the betain hydrochloride dissolved in water to make 500 cc. This corresponds to 2.5 g. of actual HCl in the water volume, or 25 mg. HCl to 5 cc. of solution.

Experiments were now made with a constant volume of liquid, weight of pepsin, weight of egg, but variable acid product, the digestions being carried uniformly through four hours. In each test the weights were as follows:

Coagulum from 1.5 g. egg albumin = 1.06 g. protein.

Pepsin 15 mg. in 30 cc. solution.

Liquid volume made always to 60 cc.

At the end of the digestion, conducted at 40°, the mixtures were boiled and filtered. The slight residues were well washed and the total filtrates used for nitrogen determinations. The volumes of betain hydrochloride solution taken contained the equivalents of 25, 50, 75, 100, 125 and 150 mg. of actual HCl and would furnish, therefore, a considerable amount of nitrogen to the filtrate. The volume in test A was 5 cc., containing 106.9 mg. of the hydrochloride and, therefore, 9.6 mg. of N. This weight is subtracted from the result of the Kjeldahl, and corresponding amounts in the other tests. The pepsin N is too small to be noted here.

The results of the Kjeldahl determinations are given below, and the values are corrected for the betain hydrochloride N. It is assumed that all the nitrogen from this source came through in the filtrate, which is probably correct for a test carried out in this manner. When neutralization is effected before filtering, however, some of the betain may be separated and precipitated with the neutralization product.

TABLE I.

| | Cc. betain HCl sol. | Total N. | Betain N. | Net N. | Protein. |
|---|---------------------------|-------------|--------------|-----------|----------|
| A | 5 | 0.0157 | 0.0096 | 0.0061 | 0.0381 |
| B | 10 | 0.0806 | 0.0192 | 0.0614 | 0.3838 |
| C | 15 | 0.1530 | 0.0288 | 0.1242 | 0.7762 |
| D | 20 | 0.1874 | 0.0384 | 0.1490 | 0.9313 |
| E | 25 | 0.1961 | 0.0480 | 0.1481 | 0.9256 |
| F | 30 | 0.2079 | 0.0575 | 0.1504 | 0.9400 |

TABLE II.

| | Mg. HCl added. | Soluble N. | Protein. |
|---|-------------------|---------------|------------|
| A | 25 | small, not | determined |
| B | 50 | 0.0980 | 0.6125 |
| C | 75 | 0.1422 | 0.8887 |
| D | 100 | 0.1410 | 0.8812 |
| E | 125 | 0.1526 | 0.9538 |
| F | 150 | 0.1618 | 1.0112 |

A parallel set of experiments was carried out, using free hydrochloric acid in place of the betain hydrochloride of Table I. The conditions of the tests were otherwise the same. It was observed that the digestions began somewhat earlier and for a time appeared to be more marked than with the betain salt. At the end of the period of four hours the extent of the digestion in the two cases was nearly the same, with the advantage slightly in favor of the free acid, as shown in Table II.

As showing, further, the rapid digestive action of the betain hydrochloride experiments were made with fibrin, as with the egg. In each test 3.9 g. of fibrin, equivalent to 1.06 g. of protein, were used. The total liquid volume was 60 cc., containing varying amounts of the betain salt and 15 mg. of pepsin. The digestion time was three hours at 40°. At the end of the time the mixtures were boiled, diluted and filtered for the Kjeldahl determinations. The results of the tests are given in Table III.

TABLE III.

| | Cc. betain HCl sol. | Total N. | Betain N. | Net N. | Protein. |
|--------|------------------------|-------------|--------------|-----------|----------|
| A..... | 5 | 0.0462 | 0.0096 | 0.0366 | 0.2287 |
| B..... | 10 | 0.1496 | 0.0192 | 0.1304 | 0.8150 |
| C..... | 15 | 0.1824 | 0.0288 | 0.1536 | 0.9600 |
| D..... | 20 | 0.1869 | 0.0384 | 0.1485 | 0.9281 |
| E..... | 25 | 0.1995 | 0.0480 | 0.1515 | 0.9468 |
| F..... | 30 | 0.2160 | 0.0575 | 0.1585 | 0.9906 |

The digestions progressed very rapidly and it is evident that the salt dissociates largely and in amount sufficient to produce a change in the protein almost comparable with that of the free acid. That some of this separated acid goes at once into combination with the protein is suggested by the following experiment:

The coagulum from 1.5 g. of egg powder, representing about 1 g. of true protein, was mixed with 30 cc. of the betain HCl solution containing 150 mg. of the acid. The mixture was shaken through two hours to effect complete combination. (Data to be given in another paper will show something about the rapidity of combination of weak acid with protein.) At the end of the shaking, the mixture was filtered and the solid residue washed with about 30 cc. of water. The filtrate, titrated by aid of methyl orange, required 22.6 cc. of 0.1 *N* NaOH, while 30 cc. of the original required 40.8 cc. Therefore, 40.8 — 22.6 = 18.2 measures the acid held, about 66.4 mg., for the gram of protein. This is essentially the amount which would have been taken up from a weak solution of free hydrochloric acid.

In two similar experiments portions of coagulum from 1.5 g. of egg were mixed with 20 cc. of the betain hydrochloride solution and 50 cc. of water and shaken through one hour, but not as actively as before. The mixtures were filtered, the residues being washed as before. In one filtrate the HCl required 19.6 cc. of 0.1 *N* silver nitrate equal to 71.5 mg. of the acid, while in the other filtrate 19.5 cc. of 0.1 *N* NaOH were needed to neutralize the acid. The results agree in showing that 28.5 mg. of HCl had been taken by the protein in this case, where the original concentration of the acid was much stronger than in the first test.

It is desirable to know the actual concentration of the active hydrochloric acid in these solutions used for the digestion experiments, that is, the [H] concentration. Attempts were made to determine this in two ways: First, by the use of a series of indicators as suggested by Frieden-thal, Salm and others, and perfected by Soerensen and second, by the measurement of the electric potential in concentration cells. This method seems to give much better results than could be secured by the indicator titrations and was finally followed for all the tests. Cells of the Ham-

burger type were used for a time, but were later given up in favor of the Hasselbalch cell and the 0.1 *N* calomel electrode, as recommended by Soerensen.¹ The much easier correction for the diffusion potential is a point of great practical importance here, and for this purpose observations were made with 3.5 *N* and 1.75 *N* KCl, as a connecting bridge between the concentration cell and the calomel electrode.

For the sake of comparison and to test the general accuracy of the method I made a series of determinations of π_0 , the potential of a true normal solution, at 18°, following the Soerensen procedure. This I found to be = 0.3381 at 18°, and about 0.3379 at 20°, which is a trifle higher than the Soerensen value, *viz.*, 0.3377. I kept the temperature as nearly as possible at 20° during the tests, and therefore took

$$P_H = (\pi - 0.3379)/0.0582$$

as the formula for reduction generally employed. For higher temperatures the denominator is a little larger and is practically 0.0002 more for each degree. (The whole denominator is 0.0001987 T , where T is the absolute temperature.) As the P_H is the common logarithm of the reciprocal value of the $[H]$ concentrations of the solutions, the latter is easily calculated.

Determinations made on the solutions of the same strength as were employed in the digestion experiments gave these results. The figures given under "theory" show the $[H]$ concentrations on the assumption that the HCl is fully separated from the salt and completely dissociated.

TABLE IV.

| | Cc. betain HCl sol. | H ₂ O. | P_H . | C_H . | Theory C_H . |
|--------|------------------------|-------------------|---------|---------|-------------------|
| A..... | 5 | 55 | 2.067 | 0.0085 | 0.0114 |
| B..... | 10 | 50 | 1.868 | 0.0135 | 0.0228 |
| C..... | 15 | 45 | 1.753 | 0.0176 | 0.0343 |
| D..... | 20 | 40 | 1.656 | 0.0220 | 0.0456 |
| E..... | 25 | 35 | 1.592 | 0.0256 | 0.0571 |
| F..... | 30 | 30 | 1.534 | 0.0292 | 0.0686 |

The experimental results are very interesting. The weakest solution is slightly more than 0.01 *N*, while the strongest is less than 0.1 *N*. It must be remembered that the betain hydrochloride is dissolved so as to make in 5 cc. the equivalent of 25 mg. of HCl, and each solution was diluted to 60 cc. with pure water before each test. As the dissociation in the 0.01 *N* HCl is not far from 95%, it will be seen that in the weakest solution the $[H]$ of the mixture is about 85% of the theoretical. In the strongest solution, the $[H]$ concentration is about 46% of the theoretical.

Several determinations were made of the concentration of the $[H]$ in the acid liquid standing over egg coagulum at the outset of digestion, or before pepsin is added. Two tests are sufficient to illustrate this con-

¹ *Biochem. Z.*, 21, 131 (1909); *Ergeb. der Phys.*, 12, 393 (1912).

dition. In the first, 10 cc. of the above betain hydrochloride solution (= 50 mg. HCl) were mixed with 50 cc. water and the coagulum from 1.5 g. of egg. In the second case 30 cc. of the same acid solution were mixed with 30 cc. of water and the 1.5 g. of egg. The mixtures stood two hours with frequent shaking and were then filtered. The potential tests were made on the filtrates, with these results:

| Cc. | P _H . | C _H . |
|-----|------------------|------------------|
| 10 | 2.259 | 0.0055 |
| 30 | 1.745 | 0.0179 |

In the first case the concentration of the acid left is about what comes from the dissociation of a protein hydrochloride in excess of water. In the second case the hydrogen ion concentration is reduced to that of an original solution of 15 cc. of the betain hydrochloride. The gram of protein has taken up approximately 7% of acid and the supernatant liquid exhibits clearly the excess.

In ordinary digestion experiments in which a protein-like egg albumin is dissolved by pepsin and hydrochloric acid, the concentration as well as the total amount of the latter come into play. We speak of a 0.2% acid as being a good concentration, and this is true, provided the total amount of acid is more than enough to combine with all the protein. In the usual test to measure the activity of pepsin, as given in the U. S. Pharmacopeia, for example, we have a mixture containing about 1.25 g. of real protein with one-tenth its weight of actual HCl in 40 cc. of liquid. The original concentration of the acid is therefore about 0.3%, but approximately one-half of this is taken up by the protein, leaving a residual concentration of 0.15%, which is probably more than is required for maximum activity. From the experiments above with betain hydrochloride, as well as with free HCl, it is seen that digestion is rapid in a far lower concentration.

II. The Behavior of Glutaminic Acid Hydrochloride.

For the experiments here, I used a pure preparation made in the laboratory by the hydrolysis of casein and which, by titration of the chlorine and by a nitrogen determination, was known to be practically pure glutaminic acid hydrochloride, $\text{COOH} \cdot \text{CH}_2\text{CH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH} \cdot \text{HCl}$. The salt is readily soluble in water and 500 mg. required 54.5 cc. 0.1 *N* NaOH for titration with phenolphthalein. This measures the hydrochloric acid and one carboxyl group.

Preliminary experiments showed that solutions of this hydrochloride in presence of pepsin digested egg and fibrin rather rapidly. In the following four trials the coagulum from 1.2 g. of egg was used in A and B, and 5 g. of prepared fibrin in C and D. In each case 50 mg. of pepsin, 600 mg. of glutaminic acid hydrochloride and 50 cc. of water were used. The mixtures were digested at 40° over night. At the end of two hours the

disintegration was far advanced, and apparently complete over night. Blank experiments were made by using killed pepsin to correspond to each case. The mixtures were boiled, filtered, the filters washed and the filtrates used for nitrogen tests.

TABLE V.

| | Total N. | Blank N. | Net N. | Protein. |
|--------|-------------|-------------|-----------|----------|
| A..... | 0.1568 | 0.0358 | 0.1230 | 0.7687 |
| B..... | 0.1638 | 0.0338 | 0.1300 | 0.8125 |
| C..... | 0.2471 | 0.0357 | 0.2114 | 1.3212 |
| D..... | 0.2541 | 0.0357 | 0.2184 | 1.3650 |

The whole of the nitrogen of the pepsin and of the hydrochloride should appear in the blank and should be nearly 50 mg. But it is evident that, with the capture of some of the hydrochloric acid by the protein, the glutaminic acid becomes less soluble and possibly precipitates to some extent. However, the total digestion seems to be from 75 to 80% of what might be theoretically expected, indicating a behavior much like that of the betain hydrochloride.

A number of digestion experiments were then made exactly as with the betain salt. A solution of glutaminic acid hydrochloride was made containing 6.285 g. to 250 cc. Five cc. of this contains 125.69 mg., or 25 mg. of HCl in combination. The N content of 5 cc. is 9.6 mg.

As in the former experiments the coagulum from 1.5 g. of egg albumin was always taken, corresponding to about 1 g. of protein. The digesting volume was always 60 cc., of which 30 cc. were made up of a pepsin solution containing 15 mg. of pepsin. The digestions were carried on through four hours at 40°, and at the end of this time the mixtures were boiled, diluted, and filtered for the nitrogen tests. The actual digestions began somewhat more slowly than with the betain hydrochloride, and evidently do not go as far. This is probably due to the fact that the hydrogen ion concentrations are lower, as will appear below. Table VI gives the result of the determinations for soluble nitrogen.

TABLE VI.

| | Cc. glut. HCl sol. | Total N. | Glut. N. | Net N. | Protein. |
|--------|-----------------------|-------------|-------------|-----------|----------|
| A..... | 5 | 0.0196 | 0.0096 | 0.0100 | 0.0625 |
| B..... | 10 | 0.0711 | 0.0192 | 0.0519 | 0.3244 |
| C..... | 15 | 0.1211 | 0.0288 | 0.0923 | 0.5769 |
| D..... | 20 | lost | 0.0384 | .. | .. |
| E..... | 25 | 0.1765 | 0.0480 | 0.1285 | 0.8051 |
| F..... | 30 | 0.1894 | 0.0575 | 0.1319 | 0.8244 |

It is seen that these digestion values are not as high as were found in the case of the other hydrochloride and the table to be given below will afford a possible explanation of this. Some of the same solution was employed for determination of the hydrogen concentration at 20°, as de-

scribed for the experiments with the betain hydrochloride. Table VII below gives the numerical values.

TABLE VII.

| | Cc. glut. ac. HCl sol. | H ₂ O. | P _H . | C _H . | Theory C _H . |
|--------|---------------------------|-------------------|------------------|------------------|----------------------------|
| A..... | 5 | 55 | 2.216 | 0.0060 | 0.0114 |
| B..... | 10 | 50 | 2.010 | 0.0097 | 0.0228 |
| C..... | 15 | 45 | 1.908 | 0.0123 | 0.0343 |
| D..... | 20 | 40 | 1.852 | 0.0140 | 0.0456 |
| E..... | 25 | 35 | 1.811 | 0.0154 | 0.0571 |
| F..... | 30 | 30 | 1.785 | 0.0164 | 0.0686 |

It is plain that we have, in all the dilutions, a lower hydrogen concentration than was the case with the betain salt. In the last mixture, equivalent to 150 mg. of hydrochloric acid in the 60 cc., the concentration is but little over half that of the corresponding betain hydrochloride. This difference undoubtedly accounts for the lower digesting activity observed in the experiment.

The [H] concentrations observed here are practically all due to the dissociation of the inorganic acid, as the dissociation of the glutaminic acid is very low. The residual concentrations of similar solutions, standing over egg albumin, were found to be very trifling in a number of experiments similar to those carried out for free hydrochloric acid to be referred to below.

III. The Behavior of Protein Hydrochloride.

In the foregoing we have seen the behavior of hydrochloric acid combined with small groups comparable to the component structures of the protein molecule itself. The acid unites readily with the complex protein, as it does with the amino acid derivatives, and the question of its physiological action here now comes up. In the therapeutic use of hydrochloric acid it is usually administered in the form of diluted solutions of the free acid, and the only important objection to this is the strongly acid taste. To overcome this objection such bodies as the betain hydrochloride have found favor and it has been shown above that a marked digestive activity is actually present with them. Combinations of proteins and hydrochloric acid have also come into use in recent years, and for these claims of acid strength are made. The experiments to be given below are intended to throw light on this point.

In the investigations I used a form of acid albumin obtained by adding hydrochloric acid to egg albumin and evaporating to dryness at a low temperature. The dry substance was powdered and mixed with enough more albumin powder to bring the HCl content to exactly 5%. The product has a strong acid taste and is only partly soluble in water. The nitrogen content was found to be 12.25%, but when the product is shaken up in water the amount of nitrogen dissolved is not large. Two experi-

ments illustrate this: Two portions of 2 g. were shaken up with 100 cc. of water and incubated at 40° through six hours. To one of these portions 50 mg. of killed pepsin had been added. At the end of the time the liquids were filtered and on the filtrates nitrogen determinations were made.

| | Total N. | Sol. N. | Pepsin N. | Net N. |
|--------|----------|---------|-----------|--------|
| A..... | 0.245 | 0.0196 | .. | 0.0196 |
| B..... | 0.245 | 0.0209 | 0.0008 | 0.0201 |

While not a large proportion of the protein is soluble, an appreciable amount of the acid dissociates and may be obtained in the clear filtrate. This is best shown by starting with a larger weight of the powder. 10 g. were shaken up with 250 cc. of water and allowed to settle over night. Part of the supernatant liquid was filtered off and portions of 10 cc. were titrated with 0.1 N NaOH.

10 cc. with methyl orange require 1.1 cc. = 100 mg. HCl for whole.

10 cc. with phenolphthalein require 1.7 cc. = 155 mg. HCl for whole.

This result shows that while some of the acid comes through combined with protein, some must be considered as existing in the form of free acid. This amounts to about 20% of the whole acid in the substance shaken up with water.

In the presence of pepsin the mixture undergoes rather a slow digestion, and the amount of hydrochloric acid now found in the filtrate is increased, but not greatly as the digestion is incomplete. This is shown by Table VIII where the effect of adding more protein is also brought out. In these experiments 2 g. of the powder and 50 mg. of pepsin were added to 100 cc. of water and digested through six hours at 40°. In some of the cases the coagulum from egg powder with 70% of real protein, and fibrin with 29% of real protein, was added. The results were as follows:

TABLE VIII.

| | Prot. HCl. G. | Added pepsin. Mg. | Added Protein. | | Sol. N. | Protein. |
|--------|---------------------|-------------------------|----------------|--------|------------|----------|
| | | | G. | | | |
| A..... | 2 | .. | ... | ... | 0.0196 | 0.1226 |
| B..... | 2 | 50 | ... | ... | 0.1472 | 0.9200 |
| C..... | 2 | 50 | 1 | egg | 0.1117 | 0.6981 |
| D..... | 2 | 50 | 2 | egg | 0.0790 | 0.4936 |
| E..... | 2 | 50 | 2 | fibrin | 0.1260 | 0.7875 |
| F..... | 2 | 50 | 3 | fibrin | 0.1142 | 0.6937 |
| G..... | 2 | 50 | 5 | fibrin | 0.0825 | 0.5156 |

The protein in the 2 g. of the powder used above amounts to about 1.53 g. Slightly over 60% of this digests when no more protein is present, but the addition of either egg or fibrin brings the digested amount down to a much lower figure. With increasing amounts of added protein the digested fraction progressively diminishes. This is undoubtedly because of the binding of the hydrochloric acid. In similar experiments with

other amounts of protein added, no greater weight of protein was digested. It appears, therefore, that acid held in this way is not capable of insuring an active digestion, even of its own protein.

The concentration of the dissociated hydrochloric acid is very low in the mixture of the powder with water. This was observed with the mixture made by adding 10 g. of the powder to water enough to make 250 cc. of solution. The mixture was well shaken through an hour and allowed to stand over night. The acid strength was determined in a cell of the Hamburger type against 0.1 N HCl. The result was found, $C_H = 0.00726$. The insoluble residue was again shaken with water and allowed to stand. The supernatant liquid gave a lower acid value than before. This operation was repeated twice. The results of the four trials were as follows, showing for the H concentrations:

1st water, 0.00726; 2nd water, 0.00517; 3rd water, 0.00483; 4th water, 0.00352.

Assuming the hydrochloric acid to be all split off in the first water treatment the concentration should be 0.0548, or with 95% dissociated 0.05296. The amount of free acid available for activation of pepsin is, therefore, but a fraction of that split off from the betain hydrochloride. A preparation of this character is sold under the name of *oxynin* as a hydrochloric acid substitute.

This holding of the HCl by protein is shown easily in another way, using moist, freshly coagulated egg albumin as a substratum. I made a series of experiments in which different amounts of coagulated egg were mixed with 150 cc. of N/15 HCl and either digested through a certain time or allowed to stand some hours before testing. In all cases the character of the liquid standing over any remaining albumin was determined. The volume of this liquid which could be filtered off was found. The results of experiments are given in Table IX.

TABLE IX.

| | A. | B. | C. | D. | E. | F. | G. |
|------------|----------|----------|----------|----------|-------------|-------------|-----------|
| Coag. from | 5 | 6 | 8 | 10 | 5 | 10 | 15 g. egg |
| Treatment | Digested | Digested | Digested | Digested | Not digest. | Not digest. | Digested |
| Vol. filt. | 149 cc. | 146 cc. | 138 cc. | 135 cc. | ... | ... | 100 cc. |

In A, B, C, D, and G the digestions were carried through 4 hours at 50°, with the addition of 50 mg. of pepsin. In A and B practically all of the protein went into solution before the end of the period. In C some was left which held a little of the digesting liquid and in D the amount was still greater. In G the portion digested was apparently very slight and the volume of liquid which ran through the filter was much less. The weights of actual protein, and acid added, expressed in percentages of the protein weight, are as follows:

TABLE X.

| | A. | B. | C. | D. | E. | F. | G. |
|--------------------------|-------|------|------|------|-------|------|------|
| Weight of protein, g.... | 3.5 | 4.2 | 5.6 | 7.0 | 3.5 | 7.0 | 10.5 |
| Per cent. HCl..... | 10.43 | 8.69 | 6.52 | 5.21 | 10.43 | 5.21 | 3.48 |

The potential tests in six of the undiluted filtrates, representing the real acid concentration of the supernatant liquids, gave these results:

TABLE XI.

| | A. | C. | D. | E. | F. | G. |
|----------------------|--------|--------|--------|--------|--------|--------|
| P _H | 1.696 | 2.352 | 2.636 | 1.403 | 1.763 | 2.957 |
| C _H | 0.0201 | 0.0044 | 0.0023 | 0.0396 | 0.0173 | 0.0011 |

In A an appreciable amount of free acid is found in the liquid after digestion, while in E, of the same original strength but not digested, the free acid concentration is nearly twice as great. In C there is scarcely enough acid for proper digestion, while in D there was an appreciable amount of albumin left. In G the acid concentration was far too low for digestion, as most of the egg remained undissolved. What passed through the filter was merely acid albumin. In E and F there was, of course, no digestion and very little solution. The amounts of free acid were consequently higher here.

After making the potential tests some of the liquids were returned to the original filtrates and mixed with wash water sufficient to bring all the volumes up to 250 cc. In this way practically everything soluble was washed out of the filters. 25 cc. portions of the filtrates were titrated with 0.1 *N* alkali and with 0.1 *N* silver nitrate, after separation of albumin, with the following results:

TABLE XII.

| | NaOH with methyl orange. | NaOH with phenol phthalein. | NaOH formal- titration. | AgNO ₃ ti- tration. | Per cent. of HCl recovered. |
|--------|-----------------------------------|--------------------------------------|-------------------------------|-----------------------------------|-----------------------------------|
| A..... | Ca 6 cc. | 12.2 | 14.0 | 9.7 | 97 |
| B..... | Ca 3 cc. | 13.0 | 15.4 | 9.2 | 92 |
| C..... | Trace | 12.8 | 15.5 | 8.6 | 86 |
| D..... | o | 13.0 | 15.4 | 8.6 | 86 |
| G..... | o | 5.4 | 6.5 | 3.5 | 35 |

The results with the methyl orange titration were far from sharp, as is always the case in presence of partly digested protein, and merely give an indication of the practical absence of free hydrochloric acid in three of the cases. Figures showing the results of the formaldehyde titration are also added, but they show no marked increase of protein products in the digestion filtrates. No great importance can be attached to them for the further reason that the weak acid concentrations were probably not sufficient to prevent a slight bacterial action between the time of digestion and the titration. But the results of the silver nitrate determinations are interesting. If all the hydrochloric acid had passed

into the filtrates the amount of silver nitrate required would have been exactly 10 cc. in each case. But there was always a loss depending on the amount of acid held by the undigested protein. By *prolonged washing all of this acid could have been dissociated and washed out*. Such acid cannot be considered as mechanically retained, but is doubtless chemically combined. In Sample G two-thirds of the acid is so held, and here the protein residue is very large.

For the actual digestion of protein by pepsin and acid it is not necessary that the amount of free acid should be large, but there *must be some excess, if the digestion is to be at all rapid*. This slight excess may probably come in some cases as a result of dissociation. In Sample C we have about the limit of digestive action, but with the same amount of acid and double the protein there is practically no digestion in G.

These experiments are sufficient to show that combinations of protein and HCl, with not more than 5 or 6% of the latter present, can have no value as digestive agents. This amount of acid is scarcely sufficient to permit the digestion of the protein itself, to say nothing of the digestion of added protein. In this respect the protein-acid combinations are not comparable with the combinations with amino acids. In Experiment A, where the digestion is rather rapid and is practically completed in two hours, the [H] concentration was found to be $P_H = 1.696$. It is interesting to note that this value is between the limits found by Soerensen¹ for the optimum digestion of egg albumin, as measured by a quite distinct process, *viz.*, the determination of the amount of nitrogen in the digestion filtrate which may not be precipitated by stannous chloride. His optimum is given at $P_H = 1.63$. It is evident, however, that any marked increase of albumin in A would lead to a decided decrease in the digestive activity.

In these experiments I have received valuable assistance from Miss Mary Hull to whom my thanks are due.

Resume.

It has been shown in this paper that the hydrochlorides of betain and glutaminic acid dissociate in aqueous solution to sufficient extent to permit the acid to aid pepsin in the rapid digestion of egg albumin or fibrin. This behavior is probably typical of amino acid combinations in general. In the case of the betain salt the action is almost equal to that of dilute hydrochloric acid of the same gross concentration. With glutaminic acid hydrochloride the action is somewhat slower, but still marked. In either case, in the mixture of coagulated protein and the hydrochloride, a part of the HCl will leave the latter and become attached to the protein.

Mixtures made by combining hydrochloric acid with protein, in a sense

¹ *Biochem. Z.*, 21, 297 (1909).

analogous to the hydrochlorides of amino acids, are physiologically much less active. Such mixtures hold scarcely enough acid to digest themselves perfectly. If further amounts of protein are added, with pepsin, digestion becomes very slow. When the protein and hydrochloric acid are so related as to bring the $[H]$ concentration down to $P_H = 2.96$ the rate of digestion is slow. This is the case when the weight of the acid is about 3.5% of the weight of the egg albumin, and 150 cc. of $N/15$ acid is the liquid volume.

On the other hand, when the weight of the acid in 150 cc. of $N/15$ HCl is about 10% of the weight of the albumin, and the hydrogen concentration of the supernatant liquid is about $P_H = 1.69$, we have very rapid digestion. This appears to be near the maximum of activity. We find all degrees of digestive activity between these limits. Dry preparations of protein and hydrochloric acid about midway between these limits cease to be physiologically active.

NORTHWESTERN UNIVERSITY.

[FROM THE LABORATORIES OF PHYSIOLOGICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS AND JEFFERSON MEDICAL COLLEGE.]

GASTRO-INTESTINAL STUDIES. VII. THE UTILIZATION OF INGESTED PROTEIN AS INFLUENCED BY UNDERMASTICATION (BOLTING) AND OVERMASTICATION (FLETCHERIZING).

BY L. F. FOSTER AND P. B. HAWK.

Received July 18, 1914.

I. Introduction.

Within the last few years attention has been frequently called to the importance of the proper mastication of food. Campbell¹ in 1903 made the following statements:

"The primary object of mastication is to break up the food so as (1) to facilitate the swallowing of it and (2) to insure its admixture with the digestive juices, both of the mouth and whole digestive canal. Mastication has other far-reaching effects. It promotes the flow of saliva, secures proper insalivation of food, increases the quantity of alkaline saliva passing into the stomach, stimulates the heart and circulation, and, finally, influences the nutrition of the jaws and their appendages by stimulating blood and lymph circulation. Proper mastication tends to diminish the amount of food consumed, by reducing the quantity needful to constitute a sufficiency, for the more perfectly a food is chewed the more perfectly is it digested and the more economically is it disposed of in the system. Insufficient mastication is the cause, direct or indirect, of many evils. It may cause local irritation resulting in acute gastritis; appendicitis is believed by Sir Frederick Treves to be due directly to food bolting, gastric intestinal catarrh may be induced through the action of certain toxins; gastric secretion may be checked through paralysis of stomach nerves, while the teeth and jaw structures are underdeveloped and disposed to disease."

¹ *Lancet*, July 11, 1903.

Chittenden¹ has stated that thorough mastication of food is a material aid to digestion which is to take place in the stomach and intestine. Metchnikoff,² on the other hand, argued that it is harmful to chew food too long and to swallow it only after it has been kept in the mouth a considerable time. A disease known in America as "Bradyphagia" has arisen from the habit of eating too slowly. Einhorn³ found that the disease is rapidly cured when the patients make up their minds to eat more quickly. According to Brown⁴ the importance of chewing with reference to protein foods at least, has been grossly overestimated. He has emphasized that all high-protein feeding animals bolt their food.

In recent years the advantages of eating slowly and chewing thoroughly have been suggested by Horace Fletcher⁵ and his associates. As a result the term, fletcherism, has crept into our language. Experimental work undertaken by Chittenden, Fletcher and others has shown that by practicing thorough mastication man can, for a time at least, maintain his life processes normally on a supply of protein food less than one-half as large as that prescribed by the so-called standard dietaries.

2. Description.

Purpose and Plan.—The purpose of this investigation was to study the utilization of a typical protein as influenced by different degrees of mastication. The experiment was conducted upon two young men and consisted of four seven-day periods as follows: (1) Preliminary normal, during which the food was masticated normally; (2) bolting, in which the meat was swallowed with no attempt at mastication; (3) fletcherizing, when the food was chewed until carried down the oesophagus by the "swallowing impulse;" (4) final normal, in which ordinary mastication was practiced. The preliminary normal period of nine days was subdivided into a six-day and a three-day period. This is explained by the fact that the diet was increased at the beginning of the latter sub-period.

Subjects.—The subjects of this experiment were two laboratory assistants, F and J. F was a man of medium size, 22 years old and 58.3 kg. in weight. Previous to the experiment he had been on a comparatively simple protein diet. J was of larger build, 24 years of age, and weighed 63 kg. Previously, he had been ingesting a rather high protein diet at one of the local boarding clubs.

Diet.—A uniform diet of the following composition was fed throughout the experiment:

¹ Chittenden, "Nutrition of Man," New York, 1907, p. 23.

² Metchnikoff, "Prolongation of Life," New York, 1908, p. 159.

³ Einhorn, *Z. diät. u. physik. Ther.*, 8, 622 (1905).

⁴ Brown, "Parcimony in Nutrition."

⁵ H. Fletcher, "New Glutton or Epicure," New York, 1906.

TABLE I.

| Food. | Subject F. | | Subject J. | |
|----------------------|----------------------|-----------------|----------------------|-----------------|
| | Amount. G. or cc. | Nitrogen. G. | Amount. G. or cc. | Nitrogen. G. |
| Beef..... | 185 | 11.207 | 215 | 13.025 |
| Graham crackers..... | 150 | 1.932 | 150 | 1.932 |
| Milk..... | 650 | 3.309 | 800 | 4.072 |
| Butter..... | 150 | 0.155 | 150 | 0.155 |
| Water..... | 1800 | .. | 2100 | .. |
| Salt..... | 16 | .. | 2.0 | .. |
| Agar-agar..... | 10 | .. | 15 | .. |
| Total..... | .. | 16.603 | .. | 19.184 |

It is to be noted that meat contributed the major portion of the protein of the diet. The meat, which consisted of the best round steak procurable, was freed from all visible fat and connective tissue and was cut into 15 mm. cubes. It was cooked by being allowed to simmer for two and one-half hours in boiling water. After thorough mixture it was sampled for analysis, placed in pint mason jars, and autoclaved at 115° by the discontinuous method. The jars were stored in a refrigerator. Distilled water was drunk throughout the experiment. Agar-agar was added to the diet to facilitate defecation.

Methods.—Carmine was used to separate the feces of the several periods, satisfactory differentiations resulting in every instance. The carmine was taken in a gelatine capsule with the initial meal of each period. Total nitrogen was determined in foods, feces, and urine. The Kjeldahl method was employed, copper sulfate being used in the digestion. Analysis of feces was made on each individual stool, except when two or three small stools were passed within a short time, in which cases they were combined. Determinations were made in duplicate upon the fresh stools without previous drying. After defecation each stool was weighed, thoroughly mixed until uniform throughout, and transferred to a weighing bottle. As soon after as possible, samples were weighed for analysis. During the bolting period the macroscopic meat residues present in the feces were carefully removed and their nitrogen content determined separately. Urine was collected in 24 hr. periods, two-liter acid bottles being used as containers and powdered thymol added as a preservative.

Daily Routine.—The daily periods began and ended at 7.15 A.M. The daily program was as follows: 7.15 A.M., urination and defecation; 7.20, body weights without clothing; 7.45, breakfast; 12.00, luncheon; 5.00, exercise; 6.00, dinner; 10.30, bed. Defecation did not always occur before breakfast.

The daily ration was divided approximately into three equal portions, one for each meal. Subject F took 300 cc. of water with each meal. Two or three hours after each meal 300 cc. were drunk, making a total of 1800

cc. for the 24 hours. Subject J also ingested 300 cc. with each meal but took 400 cc. after meals, making a total 24-hour intake of 2100 cc. Exercise was taken at 5.00 each afternoon. This consisted either of a brisk two and a half mile walk or a twenty-minute swim. Both subjects were working especially hard on research problems throughout the experiment.

3. Experimental.

Discussion of Data.—The protein utilization was calculated by the ordinary method:

$$\frac{(\text{Nitrogen in Food} - \text{Nitrogen in Feces}) \times 100}{\text{Nitrogen in Food}} = \text{Percentage Utilization}$$

1. Subject F—Table II.—In the ordinary preliminary normal period the average daily output of fecal nitrogen was 0.759 g. This value was increased to 0.948 g. in the bolting period. The protein utilization fell from 95.43% to 94.29%. As a result of fletcherizing the food, the daily output of fecal nitrogen was lowered to 0.726 g. This was a slight decrease from the value obtained in the preliminary normal period. A correspondingly higher utilization, 95.63% was sustained during this period. In the final normal period the daily nitrogen output increased slightly to 0.765 g., a value differing but little from that of the preliminary normal period.

The results obtained are not surprising. The fine comminution of the food brought about by fletcherizing would induce its more complete utilization, thus reducing the nitrogen output in the feces. On the other hand the fact that every stool passed during the bolting period contained macroscopic meat residues seemingly indicates that the food was less efficiently utilized during this period. However, if the mean nitrogen excretion of the two normal periods is compared with that of the fletcherizing period, a slight difference of 0.036 g. of nitrogen per day is noted. Comparing in the same way the protein utilization we note that the increase is but 0.22% in favor of fletcherism. It may be concluded that even though meat residues of macroscopic size were found in the feces passed during undermastication, the total amount of meat residues was but slightly in excess of that in the normal feces.

Passing to the urinary data, the average daily nitrogen excretion of 16.369 g., during the preliminary period fell to 16.229 g., in the bolting period. This value rose to 16.697 g., in the fletcherizing period and fell to 16.639 g. in the final normal period.

The decreased urinary nitrogen excretion during food bolting might be explained by the fact that less of the ingested protein was hydrolytically split by the digestive juices. The increased output of fecal nitrogen coupled with the appearance of macroscopic meat residues in all stools from this period, lends support to this explanation. The fine division

TABLE II.
Subject F.

| Day. | Urine. Vol. cc. | Body wt. Kg. | Weight stool. | Total nitrogen. (G.) | | N balance. G. | N absorbed. G. | Utiliza- tion. %. |
|----------------------------|--------------------|-----------------|------------------|----------------------|---------------|------------------|-------------------|-------------------------|
| | | | | Food. | Feces. Urine. | | | |
| Preliminary Normal 3 days. | | | | | | | | |
| 1 | 1200 | 58.36 | 95.5 | 16.603-0.759 | 16.712 | -0.868 | .. | ... |
| 2 | 1568 | 58.38 | 127.0 | | 16.351 | -0.507 | .. | ... |
| 3 | 1635 | 58.37 | 153.5 | | 16.044 | -0.200 | .. | ... |
| Average..... | | | 94.0 | | 16.369 | -0.525 | 15.844 | 95.43 |
| Bolting 7 days. | | | | | | | | |
| 1 | 1820 | 58.12 | 94.0 | 16.603-0.948 | 15.511 | +0.144 | .. | ... |
| 2 | 1580 | 57.94 | 121.5 | | 16.273 | -0.618 | .. | ... |
| 3 | 1730 | 57.92 | 78.2 | | 16.312 | -0.657 | .. | ... |
| 4 | 1490 | 58.10 | 104.9 | | 16.250 | -0.595 | .. | ... |
| 5 | 1335 | 57.90 | 224.0 | | 16.869 | -1.214 | .. | ... |
| 6 | 980 | 57.87 | 111.4 | | 15.956 | -0.301 | .. | ... |
| 7 | 1160 | 57.81 | ... | | 16.433 | -0.678 | .. | ... |
| Average..... | | | 90.6 | | 16.229 | -0.574 | 15.655 | 94.29 |
| Fletcherizing 7 days. | | | | | | | | |
| 1 | 1560 | 57.77 | 88.5 | 16.603-0.726 | 18.106 | -0.229 | .. | ... |
| 2 | 1530 | 57.69 | 158.0 | | 17.234 | -1.357 | .. | ... |
| 3 | 1590 | 57.54 | 76.2 | | 16.876 | -0.999 | .. | ... |
| 4 | 1410 | 57.70 | 152.4 | | 16.447 | -0.570 | .. | ... |
| 5 | 1675 | 57.46 | 115.6 | | 16.919 | -1.042 | .. | ... |
| 6 | 1220 | 57.44 | ... | | 13.748 | +2.139 | .. | ... |
| 7 | 1700 | 57.40 | ... | | 17.546 | -1.669 | .. | ... |
| Average..... | | | 84.4 | | 16.697 | -0.620 | 15.877 | 95.63 |
| Final Normal 7 days. | | | | | | | | |
| 1 | 1435 | 57.14 | 42.7 | 16.603-0.765 | 16.445 | -0.607 | .. | ... |
| 2 | 1295 | 57.07 | 120.0 | | 16.271 | -0.433 | .. | ... |
| 3 | 1560 | 57.29 | 216.5 | | 16.349 | -0.511 | .. | ... |
| 4 | 1455 | 57.23 | 114.9 | | 16.502 | -0.664 | .. | ... |
| 5 | 1868 | 57.28 | 117.3 | | 16.559 | -0.721 | .. | ... |
| 6 | 1820 | 56.78 | ... | | 16.309 | -0.471 | .. | ... |
| 7 | 1760 | 56.83 | ... | | 18.041 | -0.203 | .. | ... |
| Average..... | | | 87.3 | | 16.639 | -0.801 | 15.838 | 95.39 |

of the meat by fletcherism, on the other hand, probably induced the splitting of a larger quantity of protein by the digestive juices, and this in turn resulted in the appearance of an increased amount of exogenous nitrogen in the urine. As the daily nitrogen excretion was slightly higher during the final than in the preliminary normal period, it may be concluded that the effect of fletcherizing the food extended into the subsequent period.

2. Subject J—Table III.—During the preliminary normal period protein was not so well utilized as in the subsequent periods. The average

daily nitrogen output in feces was 1.306 g., the utilization being 93.19%. In the bolting period the daily nitrogen output was 1.266 g., with a utilization value of 93.41%. In the fletcherizing period the fecal nitrogen decreased, the average output being 0.906 g. per day. An accompanying increased utilization value of 95.32% was manifest. An average output of 0.919 g. was sustained during the final normal period of the experiment. The utilization was only slightly decreased, the value here being 95.21%.

TABLE III.

Subject J.

| Day. | Urine. Vol. cc. | Body wt. Kg. | Wt. stool. G. | Total nitrogen. (G.) | | | N balance. G. | N absorbed. G. | Utiliza- tion. % |
|----------------------------|-----------------------|-----------------|------------------|----------------------|--------|--------|------------------|-------------------|------------------------|
| | | | | Food. | Feces. | Urine. | | | |
| Preliminary Normal 3 days. | | | | | | | | | |
| 1 | 1690 | 63.80 | 103.5 | 19.184-1.306 | | 18.850 | -0.942 | .. | ... |
| 2 | 1707 | 63.55 | 147.0 | | | 18.798 | -0.920 | .. | ... |
| 3 | 1660 | 63.64 | 130.0 | | | 18.827 | -0.949 | .. | ... |
| Average..... | | | 126.8 | | | 18.827 | -0.949 | 17.878 | 93.19 |
| Bolting 7 days. | | | | | | | | | |
| 1 | 2110 | 63.09 | 125.5 | 19.184-1.266 | | 18.519 | -0.601 | | |
| 2 | 1760 | 63.80 | 133.5 | | | 16.073 | +1.845 | | |
| 3 | 1595 | 63.30 | 70.2 | | | 19.150 | -1.232 | | |
| 4 | 1690 | 63.10 | 146.8 | | | 18.131 | -0.213 | | |
| 5 | 1960 | 63.18 | 69.4 | | | 17.872 | +0.046 | | |
| 6 | 1834 | 62.80 | 61.5 | | | 17.841 | +0.031 | | |
| 7 | 1815 | 62.70 | ... | | | 18.345 | -0.427 | | |
| Average..... | | | 86.7 | | | 17.990 | -0.072 | 17.918 | 93.41 |
| Fletcherizing 7 days. | | | | | | | | | |
| 1 | 1850 | 62.65 | 27.4 | 19.184-0.906 | | 21.189 | -2.911 | | |
| 2 | 1640 | 62.52 | 90.0 | | | 19.946 | -1.668 | | |
| 3 | 1195 | 62.62 | 76.7 | | | 19.708 | -1.430 | | |
| 4 | 1440 | 62.75 | 141.0 | | | 20.130 | -1.852 | | |
| 5 | 1880 | 62.72 | 169.2 | | | 20.464 | -2.186 | | |
| 6 | 1707 | 62.57 | 80.5 | | | 19.845 | -1.567 | | |
| 7 | 2170 | 62.58 | ... | | | 19.557 | -1.279 | | |
| Average..... | | | 83.5 | | | 20.118 | -1.840 | 18.278 | 95.32 |
| Final Normal 7 days. | | | | | | | | | |
| 1 | 1490 | 62.23 | 40.2 | 19.184-0.919 | | 19.960 | -1.425 | | |
| 2 | 1735 | 61.88 | 247.0 | | | 20.243 | -1.926 | | |
| 3 | 1790 | 62.05 | 123.6 | | | 20.062 | -1.797 | | |
| 4 | 1910 | 62.07 | 144.5 | | | 19.745 | -1.480 | | |
| 5 | 2320 | 61.91 | 87.7 | | | 19.396 | -1.131 | | |
| 6 | 1812 | 62.05 | ... | | | 19.353 | -1.188 | | |
| 7 | 2422 | 61.76 | ... | | | 19.431 | -1.166 | | |
| Average..... | | | 92.0 | | | 19.703 | -1.438 | 18.265 | 95.21 |

The incomplete utilization of protein during the preliminary period was undoubtedly due to the extremely nervous condition of J. His diary for one of the last days of the period reports, "Much gas in my stomach, a constant taste of the meat eaten, and a general feeling of lassitude." J was constipated during the last days of the period, the final feces not appearing until the fourth day of the subsequent period. It seems reasonable to infer that under these conditions digestion was somewhat sluggish and a consequent inefficient utilization of protein resulted.

The discrepancy in protein utilization between the preliminary and final normal periods is perhaps susceptible of another interpretation. The effects of over mastication may have extended into the final period, in other words, a specific adaptation of the protein digestive juices may have been induced by the fine division of the protein through complete mastication. Neilson and Terry¹ have reported adaptations in the salivary glands of dogs. These investigators found that the saliva of dogs fed on bread exhibited stronger amylolytic power than that of meat-fed dogs. Neilson and Lewis² found evidence of adaptation in human saliva, while Simon³ reported a greater amylolytic activity in human saliva on carbohydrate diet than on either a mixed or protein diet. Mendel, Chapman and Blood,⁴ Carlson, and Chittenden,⁵ Garry,⁶ and Wohlgemuth,⁷ have failed to detect any evidence of adaptation of human saliva to diet, even as a result of years of feeding a particular diet. Walther⁸ holds that adaptation of the digestive juices may occur if a particular diet be maintained some time, while Labosov⁹ has noted lasting alterations in the gastric glands as the result of altered dietetic conditions. London and Krym¹⁰ failed to determine any specific adaptation in the intestinal secretion of dogs. London and Lukin¹¹ as well as London and Dobrowolskaja¹² failed to detect any adaptation of digestive juices as a result of feeding a particular food. A review of the literature on the subject of adaptation seems to justify the following conclusions of Mendel, Chapman and Blood:¹³

¹ *Am. J. Physiol.*, **15**, 406.

² *J. Biol. Chem.*, **4**, 501 (1908).

³ Simon, cited by Neilson and Lewis, *Loc. cit.*

⁴ Mendel, Chapman and Blood, *Collected Papers from Physiological Chemistry Laboratory of the Sheffield Scientific School.*

⁵ *Am. J. Physiol.*, **26** (1910).

⁶ *J. Biol. Chem.*, **3**, 11 (1907).

⁷ Wohlgemuth, cited by Mendel, Chapman and Blood, *Loc. cit.*

⁸ Pawlow, "The Work of the Digestive Glands," p. 43.

⁹ Pawlow, *Loc. cit.*, p. 46.

¹⁰ *Z. physiol. Chem.*, **74**, 325 (1911).

¹¹ London and Lukin, *Z. physiol. Chem.*, **68**, 366 (1910).

¹² London and Dobrowolskaja, cited by London and Krym, *Loc. cit.*

¹³ Mendel, Chapman and Blood, *Collected Papers from Physiological Chemistry Laboratory of the Sheffield Scientific School.*

"It is difficult to conceive of a sudden adaptation resulting from several days' feeding of a certain diet as advocated by the Pawlow school. The assumption of an entirely new role by a secretion or gland as the result of a few days' feeding is scarcely a biological probability."

It seems probable that in the case of J the output of fecal nitrogen and consequent protein utilization during the final period of the experiment, should be considered more nearly normal values. The slightly abnormal condition of J during the preliminary period would seem to explain his lowered utilization.

More pronounced difference in the amounts of urinary nitrogen excreted in the several periods were noted in the case of J than was true with F. The daily average of 18.827 g. in the preliminary fell to 17.990 g. in the bolting period and rose to 20.118 g. in the fletcherizing period. As in the experiment on F, a higher value in the final normal than in the preliminary normal period was noted, this output in case of J being 19.703 g. The lowered nitrogen excretion during bolting, and its marked increase during fletcherizing, possibly indicates that the degree of comminution of protein food determines, to a certain extent at least, the amount of hydrolytic cleavage by the digestive juices.

Composition of the Feces. 1. Metabolic Products.—It was formerly believed that all, or nearly all, of the nitrogen of the feces was due to undigested food. Voit¹ first showed that this was not necessarily true but that digestive juices and epithelium might leave residues Voit reached this conclusion when he found that fasting dogs eliminated a dark colored feces. The mucous membrane of the intestine by its secretion and by the abundant quantity of detached epithelium contributes essentially to the formation of feces. This follows from the finding of L. Hermann² that a clean, isolated loop of intestine collects material similar to feces.

In studies on food utilization it is important to know what part of the fecal nitrogen is metabolic in origin and what portion is due to undigested food. At present no sharp method of separation is known. Tsuboi³ has shown that on a flesh diet animals eliminate a feces consisting largely of metabolic products, the composition of which is widely different from that of the ingested meat. There was no proportionality between the amounts of nitrogen fed and the metabolic nitrogen excreted; neither did moderate amounts of nitrogen-free food appreciably alter the character of the feces. This investigator concluded that the greater part of the fecal dry matter is metabolic in origin. Rieder⁴ found more nitrogen in feces on a nitrogen-free diet than in fasting feces. Later, this same investigator, using men and dogs as subjects found an increase in the fecal nitrogen

¹ Voit, cited by Mattill and Hawk, *THIS JOURNAL*, 33, 12 (1911).

² Hermann, *Pflügers Arch.*, 46, 93 (1890).

³ *Z. Biol.*, 35, 68 (1897).

⁴ Rieder, cited by Tsuboi, *Loc. cit.*

excretion with the amount of nitrogen-free food fed. Tsuboi reported a similar finding. Rubner¹ found as much nitrogen in feces from a fluor-sugar-starch diet as the average from a meat diet. Using diets varying widely in composition, he obtained feces that differed but slightly in nitrogen content. The percentage of nitrogen in the feces was greater than in the food, except in cases of slightly utilized vegetable foods. Prausnitz² held that the composition of human feces never resembles that of ingested food, but on account of residual intestinal juices nearly always has a higher nitrogen content. This investigator also believed that human feces consist largely of residues not of ingested food but of intestinal secretions. Prausnitz reported meat residues in quantities varying from 1-3% of the moist feces, or 0.2%-1% of the ingested meat. The amount of feces, he holds, is dependent upon the character of the food, as some varieties require larger amounts of intestinal juices for digestion than others. H. Fletcher³ reports a feces of very small volume, pillular in form and almost odorless, as the result of proper mastication of food with its consequent reduction in the amount ingested.

Regarding utilization, Tsuboi⁴ maintained that previous work gave values that were too low, and concluded that, as nitrogen is continually being lost in the feces, to preserve body equilibrium it is necessary to replace this as well as the nitrogen excreted in the urine. Mendel and Fine⁵ believe that upon the ingestion of a meat diet, whose utilization as usually calculated is about 95%, the resulting feces are for the most part metabolic in origin. From the accumulated evidence it is reasonable to assume that a mixed diet gives fecal nitrogen the major quantity of which is metabolic in origin.

2. Bacteria in Feces.—It has been stated that one-third of the dry matter of human feces consists of bacteria, and at least one-half of the total nitrogen content is of bacterial origin.⁶ It is a well-known fact that the bacteria of the large intestine depend to a large extent for their nutrition upon the residues, not only of unabsorbed intestinal juices, but also of undigested protein food. Consequently, a quantitative determination of the bacterial nitrogen in feces gives no absolute value, but one that necessarily includes a portion of the nitrogen due to undigested food residues. For this reason fecal bacteria cannot, with absolute accuracy, be included as metabolic products. However, as may readily be recognized, it is impossible experimentally to make a quantitative separation of the metabolic from the non-metabolic products of feces.

¹ Rubner, cited by Tsuboi, *Loc. cit.*

² *Z. Biol.*, 35, 334 (1897).

³ H. Fletcher, "New Glutton or Epicure," New York, 1906, p. 150.

⁴ *Z. Biol.*, 35, 68 (1897).

⁵ *J. Biol. Chem.*, 11, 5 (1912).

⁶ Strasburger, cited by Mattill and Hawk, *Loc. cit.*; MacNeal, Latzer and Kerr, cited by Mattill and Hawk, *Ibid.*; Mattill and Hawk, *J. Expt Med.*, 14, 433 (1911).

3. **Estimation of Metabolic Nitrogen in Feces.**—It has been suggested that for every gram of total nitrogen in feces, 0.92 g. arise from residues of digestive juices, while the remaining 0.08 g. are due to unutilized protein food. Though this correction was not based upon any experimental data, it has been used to some extent in calculating utilization values.

To determine experimentally as nearly as possible the portion of total fecal nitrogen due to metabolic products, the method of Mendel and Fine¹ was employed. At the close of the final period of the experiment, the average daily output of feces by each subject during the four periods was calculated. A nitrogen-free diet of equal calorific value to that previously ingested was chosen. To supplement this diet an attempt was made to add agar-agar in amounts sufficient to bring the daily output of feces up to approximately the average daily output during the experiment.

Agar-agar is especially valuable in cases like the present. It gives bulk and softness to the feces and facilitates their elimination. Further,² being resistant to bacterial action it causes neither gas formation nor the production of harmful decomposition products. Though in certain of the herbivora common agar may be utilized up to 50%, Lohrlich³ found that in man it is digestible to but a very small extent. The minute quantities digested are probably hydrolyzed to galactose. The indigestibility of agar is recognized and therefore it is given in cases of constipation. Schmidt⁴ believes it to be the best form of cellulose for the correction of constipation, as it is high in hygroscopic properties, non-irritant and absolutely insoluble and unabsorbable.

The feces obtained from the nitrogen-free diet were analyzed for total nitrogen, and daily averages calculated as in the experiment proper. Corrections were applied for the nitrogen of the unutilized butter, carmine and gelatine capsule. This resultant value was subtracted from the average daily nitrogen output of each period. The difference was assumed to be the N due to unabsorbed residues of meat, and the protein utilization was calculated on this basis.

The following nitrogen-free diet was selected for determining the metabolic-nitrogen of the feces:

TABLE IV.

| | F. | | J. | |
|----------------|---------|----------|---------|----------|
| | Amount. | Grams N. | Amount. | Grams N. |
| Butter..... | 300 | 0.31 | 320 | 0.33 |
| Sugar..... | 128 | .. | 128 | .. |
| Agar-agar..... | 20 | .. | 25 | .. |
| Water..... | 2900 | .. | 3100 | .. |
| Salt..... | 1.6 | .. | 2 | .. |

¹ *J. Biol. Chem.*, 11, 5 (1912).

² Swartz, *Transactions of the Connecticut Academy of Arts and Sciences*, 16, 247 (1911).

³ Lohrlich, cited by Swartz, *Loc. cit.*

⁴ Schmidt, *Münch. Med. Wochschr.*, 41 (1905).

Assuming that the butter was 90% utilized, 10% of the butter nitrogen should appear in the feces. Correction was made for this nitrogen. The actual water ingestion was greater than during the experiment, when the subjects had been receiving milk which contained approximately 87% water. The water represented in the daily milk intake was calculated and the amount added to the original intake. The diet was ingested throughout a four-day period, during which time the usual routine of the experiment was followed as previously described.

a. Subject F.—The daily output of feces was 166.5 g., a much greater average than during the experiment. The average nitrogen content of the output was 0.5 g. No doubt this value is too high, inasmuch as the volume of feces during this period was nearly twice that obtained during the ingestion of the experimental diet and we would be justified in expecting an increase in metabolic nitrogen with an increase in bulk of the material in the intestine. The actual relationship could only be determined by a separate experiment. In Table V are found corrections for fecal nitrogen. It should be noted that after applying this high value as a correction the excretion of nitrogen in form of food residues is still approximately a quarter of a gram per day during normal mastication. The utilization percentages calculated on the basis of the above correction are of course somewhat higher than those in Table II, but undoubtedly they are more nearly correct values.

By calculating the metabolic nitrogen from a bulk of feces equal to that excreted during the experiment, proper, a smaller correction was obtained. The metabolic nitrogen was calculated by a direct proportion as follows: Daily output of feces from experimental diet: Daily output of feces from nitrogen-free diet:: Daily output of metabolic nitrogen during experiment: Daily output of nitrogen from nitrogen-free diet, or

$$89.1 : 166.5 :: M : 0.500 \quad M = 0.268 \text{ g. per day.}$$

The corrected fecal nitrogen output and the corresponding utilization values are found in Table VI. In using the correction obtained by calculation, tacit assumption is made that the content of metabolic nitrogen is proportional to the volume of feces excreted. Although there are no experimental data covering this point, it is hardly reasonable to expect that such would be the case. It is quite probable that 0.268 g. of metabolic nitrogen per day is a low value. The original value of 0.5 g. per day probably is more nearly normal, although the actual output undoubtedly lies between this and the 0.268 g. obtained by calculation.

b. Subject J.—The daily output of feces, from the nitrogen-free diet, was 124.3 g., in the case of J. As the average daily excretion during the experiment was 97.3 g., the discrepancy here was less than that manifested in the case of F. The metabolic nitrogen output and the corrected utilization percentages (Table VI) should be considered more nearly accurate

than were the corresponding values in the case of F. The calculation for metabolic nitrogen was made as previously described:

$$97.3 : 124.3 :: M : 0.552 \quad M = 0.432 \text{ g. per day.}$$

In Table VI may be found the values obtained by using this correction.

TABLE V.
CORRECTION FOR NITROGEN IN UNABSORBED BUTTER

| Day. | Weight stool. G. | Total N feces. G. | Fecal N from butter. G. | Metabolic N. G. |
|--------------|---------------------|-------------------------|-------------------------------|-----------------------|
| Subject F. | | | | |
| 1..... | 151.5 | 0.474 | 0.031 | ... |
| 2..... | 127.3 | 0.420 | 0.031 | ... |
| 3..... | 171.0 | 0.581 | 0.031 | ... |
| 4..... | 216.0 | 0.687 | 0.031 | ... |
| Average..... | 166.5 | 0.531 ¹ | 0.031 | 0.500 |
| Subject J. | | | | |
| 1..... | ... | ... | 0.033 | ... |
| 2..... | 93.3 | 0.448 | 0.033 | ... |
| 3..... | 189.5 | 0.967 | 0.033 | ... |
| 4..... | 214.5 | 0.965 | 0.033 | ... |
| Average..... | 124.3 | 0.585 ¹ | 0.033 | 0.552 |

TABLE VI.—CORRECTION FOR METABOLIC NITROGEN.

| Period. | Total N food. G. | Total N feces. G. | Metabolic N. G. | N in feces from unab- sorbed food. G. | N absorbed. G. | Utili- zation. %. |
|--------------------|------------------------|-------------------------|-----------------------|--|----------------------|-------------------------|
| Normal..... | 16.603 | 0.759 | 0.500 | 0.259 | 16.344 | 98.44 |
| Bolting..... | 16.603 | 0.948 | 0.500 | 0.448 | 16.155 | 97.30 |
| Fletcherizing..... | 16.603 | 0.726 | 0.500 | 0.226 | 16.377 | 98.64 |
| Normal..... | 16.603 | 0.765 | 0.500 | 0.265 | 16.338 | 98.40 |
| Normal..... | 19.184 | 1.306 | 0.552 | 0.754 | 18.430 | 96.07 |
| Bolting..... | 19.184 | 1.266 | 0.552 | 0.714 | 18.470 | 96.27 |
| Fletcherizing..... | 19.184 | 0.906 | 0.552 | 0.354 | 18.830 | 98.15 |
| Normal..... | 19.184 | 0.919 | 0.552 | 0.367 | 18.817 | 98.09 |

TABLE VII.—CORRECTED FECAL NITROGEN OUTPUT.

| Period. | Total N food. G. | Total N feces. G. | Meta- bolic N. G. | N in feces from unab- sorbed food. G. | N absorbed. G. | Utili- zation. %. |
|--------------------|------------------------|-------------------------|----------------------------|--|----------------------|-------------------------|
| Subject F. | | | | | | |
| Normal..... | 16.603 | 0.759 | 0.268 | 0.491 | 16.112 | 97.04 |
| Bolting..... | 16.603 | 0.948 | 0.268 | 0.680 | 15.923 | 95.39 |
| Fletcherizing..... | 16.603 | 0.726 | 0.268 | 0.458 | 16.145 | 97.24 |
| Normal..... | 16.603 | 0.765 | 0.286 | 0.497 | 16.106 | 97.01 |
| Subject J. | | | | | | |
| Normal..... | 19.184 | 1.306 | 0.432 | 0.874 | 18.310 | 95.45 |
| Bolting..... | 19.184 | 1.266 | 0.432 | 0.834 | 18.350 | 95.65 |
| Fletcherizing..... | 19.184 | 0.906 | 0.432 | 0.474 | 18.710 | 97.52 |
| Normal..... | 19.184 | 0.919 | 0.432 | 0.487 | 18.697 | 97.45 |

¹ Corrected for the nitrogen contained in capsule and in carmine.

4. General Discussion.

In establishing the digestibility of a food Best¹ has suggested that we must respect its influence on secretion; its absorption and sojourn in the stomach and intestine. It is a well-known fact that meat remains a relatively long time in the stomach. Tabler² has shown that the stomach acts as a reservoir for protein and that considerable absorption takes place there. Chittenden³ has taken this same view, although he believes that absorption is slow. Fermi⁴ found that finely hacked or well chewed meat was more easily digested by dogs than either coarsely cut or poorly chewed material. Cohnheim⁵ fed two fistulated dogs with meat, the first receiving it in finely hashed condition, the second in the form of cubes of 1-3 centimeters diameter. In the case of the first dog the material left the stomach 1 hour and 35 minutes after ingestion, 59% being digested. The meat cubes remained in the stomach of the second dog 2 hours and 31 minutes, 92% being digested. It was evident that although the cubes remained longer in the stomach, peptonization was markedly higher. Cohnheim concluded that the ingestion of finely chopped meat places more work on the intestine than on the stomach, whereas the reverse is true in case of ingestion of cubes. In one case trypsin brought into solution 0.13 g. of nitrogen; in the other 0.8 g. London and Polovzova⁶ found that with few exceptions, proteins are not absorbed in the stomach, but that most proteins are made soluble in the stomach to the extent of about 78%. 92% of this soluble material consists of proteoses and peptones, which is quickly attacked by the intestinal juices. It has been shown by Zunz⁷ that enzymes of the stomach have the ability to hydrolyze protein to peptones, proteoses, and amino acids, yet the length of time required is far in excess of that during which protein remains in the stomach.

It seems reasonable to suppose in the case of man that bolted meat would remain longer in the stomach than material which had been reduced to a state of fine division through fletcherism. Abderhalden and Meyer⁸ have demonstrated that the activity of pepsin is not necessarily confined to the stomach, but that it may be continued in the intestine. The proteins undigested in the stomach adsorb the enzyme and carry it into the intestine. Following the digestion of these proteins by the contained enzyme, this released pepsin is free to digest other proteins as well, since the reaction of the intestinal canal is often acid. It would seem from these

¹ *Deutsches Archiv. Klin. Med.*, 104, 94 (1911).

² Tabler, cited by Best, *Loc. cit.*

³ Chittenden, "Nutrition of Man," New York, 1907, p. 31.

⁴ Fermi, cited by Best, *Loc. cit.*

⁵ *Munch. Med. Wochschr.*, 54, 2582 (1907).

⁶ *Z. physiol. Chem.*, 49, 328 (1906), and 57, 113 (1908).

⁷ *Beitr. Chem. Physiol. und Path.*, 3, 339 (1903).

⁸ *Z. physiol. Chem.*, 74, 67 (1911).

findings that in food bolting, peptic digestion in the intestinal canal may have an important bearing.

Despite the claim that fletcherism¹ and the use of smaller quantities of food decrease the number of intestinal bacteria, Metchnikoff² does not agree that putrefaction is prevented. It is logical to infer that for the optimum utilization of starchy foods, habits of thorough mastication, should be encouraged with the purpose of increasing the digestion of the material at the beginning of the alimentary tract.

Concerning the utilization of meat protein, it may be concluded that the results of this investigation fail to demonstrate the advantages of fletcherism or the harmfulness of food-bolting.

5. Summary.

1. The question of the influence of mastication on the utilization of protein food was made the subject of this investigation. So far as could be determined, no work has been done on this problem; the statements of Fletcher and his associates are mainly theoretical assumptions.

2. Normal men were fed a fairly high nitrogen diet, the principal protein constituent of which was cooked beef in the form of 15 millimeter cubes. The experiment was divided into four periods: (1) Preliminary normal; (2) bolting; (3) fletcherizing; (4) final normal. Feces and urine were analyzed for total nitrogen.

3. The output of fecal nitrogen was highest during the food bolting; that during fletcherism was lowest. Protein utilization was most complete as the result of fletcherism, and least complete when bolting was practiced. The discrepancies, however, averaged only 1.6%. Utilization during fletcherism averaged 0.17% higher than during normal mastication.

4. During food bolting macroscopic meat residues appeared in every stool. In a single stool the amount was 16.5 g.

5. The fineness of the protein may determine the amount of its hydrolytic cleavage. This fact was shown by the higher nitrogen content of the urine in the fletcherizing period and the lowered output during bolting.

6. A nitrogen-free diet was fed through a four-day period at the close of the experiment proper. Total nitrogen was determined in the feces. The purpose of this was to determine as nearly as possible the average daily output of fecal metabolic nitrogen. This value was applied as a correction, and more accurate utilization data were thus obtained.

7. The fact that pepsin may be adsorbed in the stomach by particles of undigested food and carried into the small intestine to aid further in protein hydrolysis may have an important bearing on the question of the digestion of bolted meat.

¹ H. Fletcher, "The A, B, Z of our Nutrition," New York, 1904, p. 41.

² Metchnikoff, "Prolongation of Life," New York, 1908, p. 159.

8. Fletcherism of starchy foods should be encouraged so as to insure the salivary digestion of a large quantity of material.

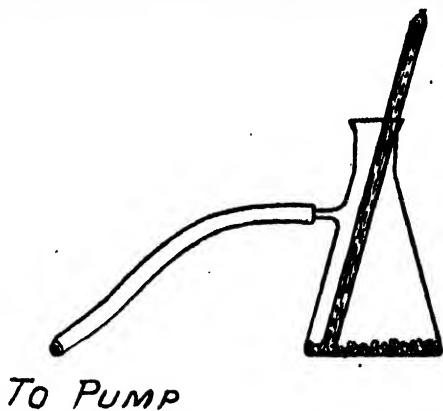
9. The results of the present experiment so far as protein utilization is concerned do not support the claims of Horace Fletcher and his followers for the efficiency of excessive mastication of food, nor do they demonstrate the harmfulness of food-bolting to the organism.

PHILADELPHIA, PA.

NOTES.

A Convenient Apparatus for Chlorination with Phosphorus Pentachloride.—The common methods employed in chlorinating solid organic compounds, such as the sulfonic acids or their metallic salts are: (1) Shake material and PCl_5 together in a flask with or without reflux condenser, some authors advocating the use of a one-hole stopper and tube for the delivery of the HCl gas just above the surface of water in a bottle or flask. (2) Grinding material and PCl_5 together in a mortar or evaporating dish.

In method (1) it is difficult to thoroughly mix the materials, and the reaction is often slow in starting. In (1) and especially in (2) the large amounts of HCl gas evolved make the use of a hood necessary and the operation unpleasant at best. In this laboratory it has been customary to perform (2) out of doors.



The authors while working on sulfonic acid derivatives devised the following simple apparatus:

The material is placed in a heavy-walled, side-neck filter flask attached to a Richards or similar filter pump. Suction is applied and the PCl_5 added. The materials are ground together with a pestle made from heavy glass rod or large tubing. No HCl fumes escape into the air, making the use of a hood unnecessary.

If but small amounts of material are available a thick-walled, side-neck test tube may be used.

The method is, of course, not applicable if the product of chlorination is volatile.

STUART P. MILLER AND FRANKLIN C. GURLEY.

LABORATORY OF ORGANIC CHEMISTRY,
MASSACHUSETTS AGRICULTURAL COLLEGE,
March 1, 1915.

The Condensation of Vanillin and Piperonal with Certain Aromatic Amines.—In a private communication J. R. Furlong calls my attention to the fact that some of the condensation products described under the above title (THIS JOURNAL, 35, 976 (1913)) were previously described by Manchot and Furlong (*Ber.*, 42, 4387). The compounds referred to are products of condensation of vanillin with *p*-aminobenzoic acid and with its ethyl ester and of piperonal with *p*-aminobenzoic acid.

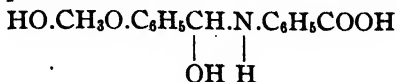
There are a number of points, however, in which our observations and conclusions are at variance and I take this opportunity to mention them.

Manchot and Furlong condensed vanillin and *p*-aminobenzoic acid in boiling alcohol, obtaining a product which was "not crystalline" and "could not be crystallized in any way." They further state that if toluene is used as solvent in the preparation that "no reaction takes place." These statements are in striking contrast to my observations, in view of the fact that I use toluene as a solvent, with or without 5% of alcohol, and obtain a very beautiful crystalline product, melting at $211-2^{\circ}$ instead of 209° , as given by Manchot and Furlong. The crystals, if formed slowly, are compact and brilliant; if formed quickly, are thin plates with sharply bevelled ends. Single crystals under the microscope appear colorless but in the mass are bright yellow. The reaction in toluene is indeed slow and the results obtained after boiling a few minutes might lead one astray. The reaction has begun, however, and is complete after boiling ten hours. Again Manchot and Furlong state that when heated with toluene, alcohol or benzene the compound breaks up, and yet I depend upon toluene for its preparation and its purification. In a special test on this point a small amount of the pure substance was dissolved in boiling toluene and cooled down. The crystals which separated had the same melting point as before. The filtrate was evaporated to dryness and only a trace of material was left. The toluene had been dried with calcium chloride. Alcohol, which Manchot and Furlong used, converts much of the compound into a varnish, even when allowed to evaporate spontaneously.

The red compound obtained by boiling the above compound in water is also in dispute. Manchot and Furlong state that it loses color at $75-7^{\circ}$ and melts at $190-200^{\circ}$. I stated that it melts at $104-6^{\circ}$ and might have added that it loses color as it re-solidifies with rising temperature and melts again at $190-200^{\circ}$. The behavior of the product when heated is, in fact, very irregular. Melting points from 84° to 106° may be obtained, depending upon the rate of heating or upon the temperature of the bath when the substance is placed in it. It is also an incomplete statement to say that it loses color at $75-7^{\circ}$ because it loses color over a wide range of temperature, even as low as 65° . The formation of the red

compound is very rapid, the same product being obtained whether the anil is boiled 5 minutes with water or one hour.

Manchot and Furlong state that in the formation of the red compound the anil has taken up water as H and OH at the double bond, thus:



I had concluded that it was water of crystallization, but Furlong objects to this explanation, saying that I offer no evidence in support of it. I reply that it seemed the natural explanation. One thinks at once of such compounds as oxalic acid which melt in their water of crystallization, lose their water and then melt again at a much higher temperature. Other compounds like copper sulfate lose their color when the water is driven off. In the case of the red products, single crystals are reddish yellow but upon losing water they are quite colorless under the microscope. Manchot and Furlong's explanation, as they say, is that assumed by Hantzsch and Schwab (*Ber.*, 34, 829), who state that benzylidene-*p*-chloraniline hydrochloride takes up a molecule of water. This is however under the influence of a soda solution cooled below 0°. And further it is to be noted the benzylidene compound has already taken up a molecule of hydrochloric acid at the nitrogen atom. The case then is not analogous. Further, according to this explanation, an unsaturated compound becomes saturated and assumes its unsaturated character just as easily. The formation of the red compound undoubtedly begins at 70°, for Manchot and Furlong obtained a red oil in water at that temperature. I find that the water can be driven out of the compound at the same or even at a lower temperature. If the modern theory is true that unsaturated compounds are in a state of strain, involving a greater difficulty in producing unsaturated compounds than in producing saturated, this reversibility should not occur.

Furlong also refers to the lower melting point, 233-4°, which I gave to the condensation product of piperonal and *p*-aminobenzoic acid, whereas he found 242°. In view of the secondary product, melting at 171-3°, obtained when toluene is the solvent, whereas the use of alcohol seems to yield no such product, the figure may be too low, although the analysis does not indicate so great a difference.

Furlong finally refers to my hope of finding isomeric compounds in this field and states that Manchot and Furlong found that the condensation product of ethyl *p*-aminobenzoate and salicylic aldehyde occurs in two forms. At a later date Manchot and Palmberg (*Ann.*, 388, 103) regarded this as a case of keto-enol isomerism but were unable to obtain any ketone derivatives such as oximes to establish their conclusion. This view was based solely on the observation that ferric chloride acts more quickly

on one form than on the other at temperatures obtained by a mixture of carbon dioxide and acetone. This leaves much to be desired in the way of characterizing the keto form.

ALVIN S. WHEELER.

UNIVERSITY OF NORTH CAROLINA.

NEW BOOKS.

The Chemistry of the Radio-Elements. Part II. By FREDERICK SODDY. Longmans, Green & Company. 44 pp. Price, \$1.75.

The second part of Soddy's well-known book deals with the radio-elements and the periodic law. In the first chapter he brings the several theories discussed in Part I, up to date, and then goes into a somewhat detailed discussion of the work of A. S. Russell, K. Fajans and A. Fleck on isotopes or the chemically nonseparable elements. It is shown that when an α -particle is expelled it carries with it two atomic charges of positive electricity, and the expulsion of these two positive charges from the atom affects the valency of the product exactly as in ordinary electrochemical changes of valency. In the case of β -particle, which is a negative electron, the loss of this single atomic charge of negative electricity increases the positive valency of the product by one. In other words, the expulsion of an α -particle causes the element to shift its position in the periodic table by two places in the direction of diminishing mass so that the product is in the family next but one; the loss of a β -particle, however, causes the element to shift its position in the periodic table by one place in the opposite direction to that for an α -ray change. A loss of one α - and two β -particles, therefore, brings the product back into the same family as the parent. These elements are found to be nonseparable chemically, and are called *isotopes*. In general terms, "whenever two or more radio-elements fall into the same place in the periodic table, then independently of all considerations as to the atomic mass, the nature of the parent element and the sequence of changes in which they result, the elements in question are chemically nonseparable and identical." It is shown that this identity probably extends to the spectrum reactions and all physical properties with the exception of mass.

The final products of the disintegration of the thorium and uranium series fall in Group IV, Family B, and have atomic weights very close to that of lead. These elements are, therefore isotopes and are chemically nonseparable. In addition, they are isotopic with Radium B, Thorium B, Actinium B and Radium D. The possibility, therefore, of lead being a mixture of two or more chemically nonseparable elements is a pertinent one. T. W. Richards and Max Lambert have recently determined the atomic weight of lead obtained from radioactive minerals, and find the atomic weight to vary from 206.40 to 206.86, a very considerable variation from the atomic weight of ordinary lead, *vis.*, 207.15. Soddy, working

independently with lead from Ceylon thorite, obtained on three determinations the figures 208.5, 208.4, 208.3. These definite confirmations of the theory are intensely interesting.

The work is well written, and should be read by every chemist.

R. B. MOORE.

Oedema and Nephritis. A Critical, Experimental and Clinical Study of the Physiology and Pathology of Water Absorption in the Living Organism. By MARTIN H. FISCHER, Eichberg Professor of Physiology in the University of Cincinnati. Second and Enlarged Edition. Pages x + 695. John Wiley and Sons, Inc. Price, \$5.00.

Although Fischer states that edema and nephritis are problems of colloid chemistry, this book from the chemical standpoint is of interest only to those who are closely associated with biological work.

The first edition received so much adverse criticism that the author advises the interested reader to examine the evidence away from the noise of the pleading attorneys. With this advice in mind, it is yet hard for the reader to dismiss the feeling that the evidence in favor of his theory is presented in attorney-like fashion and that both sides are perhaps not equally well presented.

The retention of water in the tissues in cases of edema and nephritis, he states, is due to an abnormal production or accumulation of acids in the tissues. This increases the hydration capacity of the colloids and this is the explanation of edema. Nephritis is an edema of the kidney, glaucoma an edema of the eye, uremia an edema of the nervous tissues. He is aware that other substances than acids may be a cause of water retention, but in life he thinks these are of minor importance. Among such bodies are pyridine, certain amines, urea, and alkalies. In addition to edema and nephritis Fischer would explain absorption and excretion largely by a changing acid content of the tissues.

The evidence presented in favor of his theory is both experimental and clinical. Many test-tube experiments are cited to show the influence of alkalies and especially acids on the swelling of gelatin and fibrin and the influence of salts in diminishing this hydration. This forms the basis of the treatment which he recommends in certain cases of water retention in the body. At the same time he assures some of his critics that "These long suffering and mutilated materials" are not identical with, and are far less sensitive to the action of acids than the body proteins. The reasons for his treatment are discussed at length and his test-tube experiments are amply supported by work on animals and by clinical observations.

Much of the work upon which the theory rests has been severely criticised. The test-tube experiments speak equally well in favor of either alkalies or acids; but Fischer considers the conditions of life such that an increase in alkalinity of the body must be a rare occurrence, while acidosis is rather frequent. If Fischer's explanation of the facts is accepted, his

theory rests on a firm foundation. A successful explanation of facts, however, is not proof of the validity of an hypothesis, for we know that certain facts can be explained equally well by conflicting hypotheses. Some of the criticisms directed against his work bear out this statement.

His explanation of the edema in frog experiments (pp. 175, *et seq.*) is not accepted by McClendon (*Z. physik-chem. Biologie*, Bd. I., s. 169). McClendon gives experiments to prove that a living frog will absorb more water than a dead one and that the effect of the stoppage of circulation is to decrease rather than increase the absorption of water. Only after the tissues have long been dead will acidosis increase absorption. Finally, osmotic pressure will explain the whole water absorption. All this is contrary to Fischer's teaching, and to one who has not worked on either side of the question, the explanation is adequate.

Numerous other objections have been raised. Many of these Fischer has answered either in the book or in papers to which he gives references. The most important of these have been brought forth by Moore, and by Henderson and his collaborators. Henderson states that the acid concentration required to satisfy Fischer's theory can never be reached in the living body. From the clinical side the sharpest criticism is presented by the reviewer of the first edition of the book in the "Archives of Internal Medicine," Vol. 9, page 637.

His replies to these criticisms cannot be considered as on a par with his original presentation and betray an irritability and a use of sarcasm undesirable in a scientific discussion.

The results of the application of Fischer's treatment of edema and nephritis have been severely criticised and as warmly praised. Some believe it productive of human suffering and injury; others have found it almost a panacea. In this dilemma Fischer advises the physician to treat his nephritic cases by the old approved methods. If in spite of this he thinks death imminent, Fischer's treatment, which consists of alkali, salt and glucose, may be tried. If the patient dies, the expected will have happened; if he lives, it proves nothing but may encourage a repetition of the experiment. This he thinks is all that is necessary.

The book as a whole is extremely interesting and the presentation clear. The theory advocated is simple and explains many things for which we have no other explanation. Whether or not the theory deserves the wide application Fischer gives requires corroboration. It emphasizes the great importance of the colloids in physiology and pathology and will stimulate work in this field. The work yet necessary for the acceptance or rejection of the theory will be directly responsible for a better knowledge of edema and related problems. It is worthy of the attention of all interested in biological or medical work.

HUGH MCGUIGAN.

THE JOURNAL
OF THE
American Chemical Society

with which has been incorporated the

American Chemical Journal

(Founded by Ira Remsen)

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE CHANGES OF MASS AND WEIGHT INVOLVED IN THE
FORMATION OF COMPLEX ATOMS.

[FIRST PAPER ON ATOMIC STRUCTURE.]

By WILLIAM D. HARKINS AND ERNEST D. WILSON.¹

Received April 12, 1915.

In the study of the important question of the structure and composition of the elements, it might seem that a consideration of the relations existing between the atomic weights should give results of the greatest value. Unfortunately, however, the first suggestions presented to explain the relations which probably exist were given in such a form, and were based upon such extremely inaccurate values for the atomic weights that a very considerable prejudice has been developed against similar hypotheses.

The first important hypothesis in regard to atomic weight relations appeared in two anonymous papers in the *Annals of Philosophy* for 1815 and 1816, just one hundred years ago. These papers were known to have been written by Prout, whose ideas as they were presented received the vigorous support of Thomson, considered in England as the leading chemical authority of his day; and many years later, from 1840 to 1860, they were very strongly advocated by Dumas, who made a

¹ This first paper and the second and third papers which follow form the basis for a part of a dissertation presented to the University of Chicago by Ernest D. Wilson in part fulfilment of the requirements for the Ph.D. degree.

large number of atomic weight determinations during this period. Very many other chemists, among them Gmelin, Erdmann, and Marchand, were also numbered among Prout's supporters. On the other hand, Stas, who in the beginning tried to aid Dumas in the revival of Prout's hypothesis, afterward designated it as a pure fiction, and Berzelius at all times adhered to the view that the exact atomic weights could not be determined except by experiment.

The prejudice which existed a few years ago against Prout's idea is well shown by a quotation from von Meyer's *History of Chemistry*, printed in 1906.

"During the period in which Davy and Gay-Lussac were carrying on their brilliant work, and before the star of Berzelius had attained to its full luster, a literary chemical event occurred which made a profound impression upon nearly all the chemists of that day, *viz.*, the advancement of Prout's hypothesis. This was one of the factors which materially depreciated the atomic doctrine in the eyes of many eminent investigators. On account of its influence upon the further development of the atomic theory this hypothesis must be discussed here, although it but seldom happens that an idea from which important theoretical conceptions sprang, originated in so faulty a manner as it did."

Prout's work was not, as the above quotation infers, entirely "literary," for he made a large number of experimental determinations for use in his calculations of the specific gravity of the various elements, which he assumed to exist in the gaseous form. His experiments were, according to his own statements, somewhat crude; but he also made use of the more accurate data obtained by Gay-Lussac, and his work was based upon the volume relations of gases as discovered by the French investigator.

Exactly the form in which the numerical part of Prout's hypothesis should be expressed in terms of modern atomic weights, it is difficult to say, but the principal point is that his atomic weights, which, however, are not comparable with those now used, were expressed in whole numbers, as given below in two columns taken from his table:

TABLE I.—PROUT'S TABLE OF THE MORE ACCURATELY DETERMINED ATOMIC WEIGHTS.

| Element. | Sp. gr. | Atomic weight, 2 vols. of hydrogen being 1. |
|----------|---------|--|
| H..... | 1 | 1 |
| C..... | 6 | 6 |
| N..... | 14 | 14 |
| P..... | 14 | 14 |
| O..... | 16 | 8 |
| S..... | 16 | 16 |
| Ca..... | 20 | 20 |
| Na..... | 24 | 24 |
| Fe..... | 28 | 28 |
| Zn..... | 32 | 32 |
| Cl..... | 36 | 36 |
| K..... | 40 | 40 |
| Ba..... | 70 | 70 |
| I..... | 124 | 124 |

The atomic weights thus given by Prout are within a few units of the modern values in the case of the univalent atoms and for nitrogen; but the values given for the atoms of higher valence, with the exception of nitrogen, are approximately half the present values. This would mean that according to Prout's system, since the atomic weights he gives are whole numbers, the atomic weights of the present system should be divisible by two for the atoms of higher valence, which is equivalent to the use of the hydrogen molecule instead of the atom as a unit. In this connection it may be noticed that his atomic weights are taken on the basis of "2 volumes of hydrogen being 1."

Thus, from a numerical standpoint, Prout's hypothesis does not seem to mean what is usually supposed. Expressed in terms of the composition of what he considered to be complex atoms, it is given below in his own words:

"If the views we have endeavored to advance be correct, we may also consider the πρώτη ύλη of the ancients to be realized in hydrogen, an opinion by the way, not altogether new. If we actually consider this to be the case, and further consider the specific gravities of bodies in their gaseous state to represent the number of volumes condensed into one; or, in other words, the number of the absolute weight of a single volume of the first matter which they contain, which is extremely probable, multiples in weight must also indicate multiples in volume, and *vice versa*; and the specific gravities, or absolute weights of all bodies in the gaseous state, must be multiples of the specific gravity or absolute weight of the first matter, because all bodies in a gaseous state which unite with one another, unite with reference to their volume."

While it is true that Prout had at the time when he presented it, no real foundation for his ideas, more accurate work, while it proved his system to be invalid from a purely numerical standpoint, at the same time established the fact that the atomic weights of the lighter elements, on the hydrogen basis, are much closer to whole numbers than would be likely to result from any entirely accidental method of distribution. Thus the deviations of the lighter elements are small, as will be seen by the following table:

| Element. | At. wt. H = 1. | Deviation from a whole number. |
|----------|-------------------|-----------------------------------|
| He..... | 3.97 | 0.03 |
| Li..... | 6.89 | 0.11 |
| Be..... | 9.03 | 0.03 |
| B..... | 10.91 | 0.09 |
| C..... | 11.91 | 0.09 |
| N..... | 13.90 | 0.10 |
| O..... | 15.88 | 0.12 |
| F..... | 18.85 | 0.15 |

The average of these deviations is 0.09 unit, while the theoretical deviation on the basis that the values for the atomic weights are entirely accidental, is 0.25 unit. If the first seventeen elements are used in the calculation, the average deviation is found to be 0.15 unit, while the re-

TABLE II.—DEVIATIONS OF THE ATOMIC WEIGHTS FROM WHOLE NUMBERS.

| | At. wt. H = 1. | Diff. from whole number. | Per cent. variation or the pack- ing effect. | Possible per cent. variation. | At. wt. O = 16. | Diff. from whole number. | Per cent. variation from whole no. | Prob. error in at. wts. |
|-----------------------|-------------------|-----------------------------------|---|-------------------------------------|--------------------|-----------------------------------|---|----------------------------------|
| H ¹ | 1.000 | | | | 1.0078 | +0.0078 | 0.78 | 0.0002 |
| He ² | 3.97 | −0.03 | −0.77 | 12.5 | 4.00 | 0.00 | 0.00 | 0.01 |
| Li..... | 6.89 | −0.11 | −1.62 | 7.1 | 6.94 | −0.06 | −0.86 | 0.01 |
| Be..... | 9.03 | (+0.03) | | 5.5 | 9.1 | +0.1 | (+1.11) | 0.05 |
| B..... | 10.91 | −0.09 | −0.77 | 4.5 | 11.0 | 0.00 | 0.00 | 0.05 |
| C ³ | 11.91 | −0.09 | −0.77 | 4.2 | 12.00 | 0.00 | 0.00 | 0.005 |
| N..... | 13.90 | −0.10 | −0.70 | 3.6 | 14.01 | +0.01 | +0.07 | 0.005 |
| O..... | 15.88 | −0.12 | −0.77 | 3.1 | 16.00 | 0.00 | 0.00 | 0.00 |
| F..... | 18.85 | −0.15 | −0.77 | 2.6 | 19.00 | 0.0 | 0.0 | 0.05 |
| Ne ³ | 19.85 | | | | 20.0 | | | |
| Na ⁴ | 22.82 | −0.18 | −0.77 | 2.2 | 23.00 | 0.00 | 0.00 | 0.01 |
| Mg..... | 24.13 | +0.13 | +0.55 | 2.15 | 24.32 | +0.32 | +1.33 | 0.03 |
| Al..... | 26.89 | −0.11 | −0.40 | 1.85 | 27.1 | +0.10 | +0.37 | 0.1 |
| Si..... | 28.08 | +0.08 | +0.31 | 1.78 | 28.3 | +0.30 | +1.07 | 0.1 |
| P ⁵ | 30.78 | −0.22 | −0.71 | 1.61 | 31.02 | +0.02 | +0.06 | 0.01 |
| S ⁸ | 31.82 | −0.18 | −0.56 | 1.56 | 32.07 | +0.07 | +0.22 | 0.01 |
| Cl..... | 35.19 | +0.19 | +0.54 | 1.43 | 35.46 | +0.46 | +1.31 | 0.01 |
| Ar..... | 39.57 | −0.43 | −1.07 | 1.25 | 39.88 | −0.12 | −0.30 | 0.02 |
| K..... | 38.80 | −0.20 | −0.52 | 1.28 | 39.10 | +0.10 | +0.25 | 0.01 |
| Ca..... | 39.76 | −0.24 | −0.60 | 1.25 | 40.07 | +0.07 | +0.17 | 0.03 |
| Sc..... | 43.76 | −0.24 | −0.55 | 1.14 | 44.1 | +0.10 | +0.23 | 0.2 |
| Ti..... | 47.73 | −0.27 | −0.57 | 1.04 | 48.1 | +0.10 | +0.21 | 0.1 |
| V..... | 50.61 | −0.39 | −0.77 | 0.98 | 51.0 | 0.0 | 0.0 | 0.1 |
| Cr..... | 51.60 | −0.40 | −0.77 | 0.96 | 52.0 | 0.0 | 0.0 | 0.05 |
| Mn..... | 54.50 | −0.50 | −0.90 | 0.90 | 54.93 | −0.07 | −0.13 | 0.05 |
| Fe..... | 55.41 | −0.59 | −1.06 | 0.89 | 55.84 | −0.16 | −0.29 | 0.03 |
| Co..... | 58.51 | −0.49 | −0.83 | 0.85 | 58.97 | −0.03 | −0.05 | 0.02 |

Per cent. variation of 21 elements (omitting Be, Mg, Si, Cl), or the packing effect = 0.77%

Average deviation of the atomic weights, H = 1, from whole numbers = 0.21

Theoretical deviation of atomic weights from whole numbers on the basis that the deviations are entirely accidental = 0.25

Average deviation of the atomic weights, H = 1, for the eight elements from helium to sodium = 0.11

Average deviation of the atomic weights, O = 16, when Mg, Si, and Cl are omitted = 0.05

Average deviation of the atomic weights, O = 16, for the eight elements from helium to sodium = 0.02

¹ W. A. Noyes ("A Text-book of Chemistry," p. 72) states that the atomic weight used for hydrogen, 1.0078, is probably not in error by so much as 1 part in 5000.

² Heuse (*Verh. deut. physik. Ges.*, 15, 518 (1913)) obtained the value 4.002 as the result of 7 experiments.

³ Leduc (*Compt. rend.*, 158, 864 (1914)) gives the atomic weight of neon as 20.15 when hydrogen is taken as 1.0075. Leduc's value is not used, on account of the discovery of the complexity of neon as described in the text of the paper.

⁴ Richards and Hoover (*THIS JOURNAL*, 37, 95 (1915)) determined the atomic weights of carbon as 12.005, and of sodium as 22.995, and in Vol. 37, p. 108, they give the atomic weight of sulfur as 32.06.

⁵ The atomic weight for phosphorus is taken as 31.02 from recent determinations made by Baxter (*THIS JOURNAL*, 33, 1657 (1912)).

sult obtained for twenty-five elements is 0.21. The more complete table, designated as Table II, gives these deviations, which are seen to be negative in almost every case, the exceptions being magnesium, silicon, and chlorine. The exclusion of beryllium from consideration in this connection is due to the fact that its atomic weight is not known with sufficient accuracy, and neon is not taken into account, since its positive variation may be explained by the discovery by Thomson and by Aston that neon is a mixture of two isotopes of atomic weights twenty and twenty-two.

Not only is the variation from a whole number a negative number, but in addition its numerical value is nearly constant, the average value for the 21 elements being 0.77%, while the six elements from boron to sodium show values of 0.77, 0.77, 0.70, 0.77, 0.77, and 0.77%. The deviation is therefore not a periodic, but a constant one. If, then, a modification of Prout's hypothesis that the elements are built up of hydrogen atoms as units is to be taken as a working basis, it becomes important to find a cause for the decrease in weight which would result from the formation of a complex atom from a number of hydrogen atoms. The regularity in the effect suggests that, in general, this decrease in weight is probably due to some common cause, though the exceptional cases of magnesium, silicon, and chlorine, show that there is certainly some other complicating factor. The discovery of the reason for the deviation of the same kind in the case of neon, where it is due to its admixture with an isotope of higher atomic weight, suggests that it may not be impossible to find explanations for these three other exceptions. In order to have a term for the percentage decrease in weight, it may be well to call this the packing effect, or the percentage variation from the commonly assumed law of summation, that the mass of the atom is equal to the sum of the masses of its parts.

It has formerly seemed difficult to explain why the atomic weights referred to that of oxygen as 16 are so much closer to whole numbers than those referred to that of hydrogen as one, but, the explanation is a very simple one when the facts of the case are considered. The closeness of the atomic weights on the oxygen basis to whole numbers, is indeed extremely remarkable. Thus for the eight elements from helium to sodium the average deviation is only 0.02 unit, which is less than the average probable error in the atomic weight determinations. When twenty-one elements are taken from the table, omitting the exceptional cases of magnesium, silicon, and chlorine, the deviation averages only 0.05 unit, while if these are included, this is increased only to 0.09 unit. These results have been calculated without taking the sign into account. If the sign is considered the average deviation is reduced to 0.01 unit for the twenty-one elements. The probability that such values

could be obtained by accident, is so slight as to be unworthy of consideration. If an oxygen atom is a structure built up from 16 hydrogen atoms, then the weight according to the law of summation should be 16 times 1.0078 or 16.125. The difference between 16.125 and 16.00 is the value of the packing effect, and if this effect were the same for all of the elements, except hydrogen, then the choice of a whole number at the atomic weight of any one of them, would, of necessity, cause all of the other atomic weights to be whole numbers. Though this is not quite true, it is seen that the packing effect for oxygen is 0.77%, which is the average of the packing effects for the other 21 elements considered. Therefore, those elements which have packing effects equal to that of oxygen will have whole numbers for their atomic weights, and since the other elements show nearly the same percentage effect, their atomic weights must also lie close to whole numbers.

According to this view, Prout's hypothesis from the purely numerical standpoint, is entirely invalid, but there still remains the problem of finding an explanation for three facts: First, that the atomic weights of the lighter elements on the hydrogen basis approximate whole numbers; second, that the deviations from whole numbers are negative; and third, that the deviations are practically constant in magnitude. Before considering any explanation of these facts it is of interest to consider the following extremely interesting comments upon this subject, as written by Marignac in 1860:

"We are then able to say of Prout's hypothesis that which we can say of the laws of Mariotte and Gay-Lussac relative to the variations of the volumes of gases. These laws long considered as absolute, have been found to be inexact when subjected to experiments of so precise a nature as those of M. Regnault, M. Magnus, etc. Nevertheless they will be always considered as expressing natural laws, either from the practical point of view, for they allow the change of volume of gases to be calculated in the majority of cases, with a sufficiently close approximation, or even from the theoretical point of view, for they most probably give the normal law of changes of volume, when allowance has been made for some perturbing influences which may be discovered later, and for which it may also be possible to calculate the effects. We may believe that the same is true with respect to Prout's law; if it is not strictly confirmed by experiment, it appears nevertheless to express the relation between simple bodies with sufficient accuracy for the practical calculations of the chemist, and perhaps also the normal relationship which ought to exist among these weights, when allowance is made for some perturbing causes, the research for which should exercise the capacity and imagination of chemists. Should we not, for example, quite in keeping with the fundamental principle of this law, that is to say, in admitting the hypothesis of the unity of matter, be able to make the following supposition, to which I attach no further importance than that of showing that we may be able to explain the discordance which exists between the experimental results and the direct consequences of this principle? May we not be able to suppose that the unknown cause (probably differing from the physical and chemical agents known to us), which has determined certain groupings of primordial matter so as to give birth to our simple chemical atoms, and to impress upon each of these groups a special character and peculiar properties, has been able at

the same time to exercise an influence upon the manner in which these groups of atoms obey the law of universal attraction, so that the weight of each of them is not exactly the sum of the weights of the primordial atoms which constitute it?"

It has usually been assumed, and without any really logical basis for the assumption, that if a complex atom is made up by the union of simple atoms, the mass of the complex atom must be exactly equal to the masses of the simple atoms entering into its structure. Rutherford, from data on the scattering of α -rays in passing through gold leaf, has calculated an *upper* limit for the radius of the nucleus of a gold atom as 3.4×10^{-12} cm. The mass of this relatively heavy atom is, according to this calculation, practically all concentrated in this extremely small space, which is so small that it could no longer be expected that the mass of such a nucleus, if complex, would be equal to the sum of the masses of its component parts. In fact, since the electromagnetic fields of the electrons would be so extremely closely intermingled in the nucleus, it would seem more reasonable to suppose that the mass of the whole would not be equal to the sum of the masses of its parts. The deviation from the law of summation cannot be calculated on a theoretical basis, but it can easily be determined from the atomic weights, if the assumption is made that the heavier atoms are condensation products of the lightest of the ordinary elements, that is of hydrogen. This deviation expressed in terms of the percentage change, is what has already been determined, and designated as the packing effect.

Since this packing effect represents a decrease in weight, the first problem which represents itself for determination is the *sign* of the effect which would result from the formation of the positively charged nucleus of an atom by the combining of positive and negative electrons into some form of structure. Richardson¹ suggests that the positive nucleus of an atom might be built up of positive electrons alone and still be stable if the law of force between them were

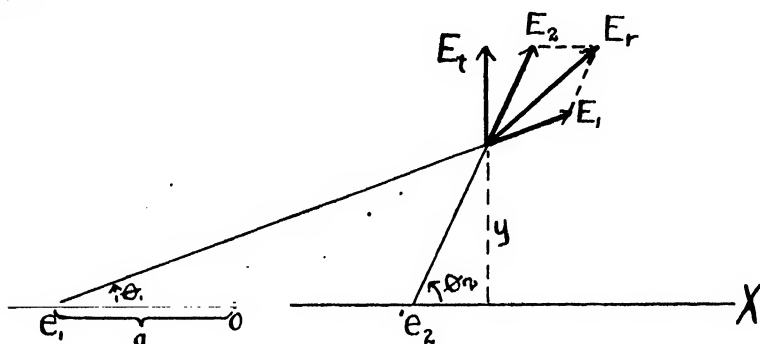
$$+ a/r^2 - b/r^{p_1} + c/r^{p_2}, \text{ where } p_2 > p_1 > 2.$$

Here the first term gives the usual law of force, the second causes the electrons when close together to attract each other, and the third expresses the repulsion which keeps them from joining together. It would, however, seem more simple to assume, what seems much more probable, that the nucleus is held together by the attraction of positive and negative electrons, both of which are assumed to be present in any complex nucleus.

Since, even when the mass is assumed to be entirely electromagnetic, there still remain two possibilities even for the simple case of hydrogen, first, that the hydrogen nucleus is the positive electron, and second, that it may be complex, it has seemed best to choose for the purpose of cal-

¹ "The Electron Theory of Matter," p. 582.

ulation the simplest system, which consists of one positive and one negative electron. The problem thus presented for solution is the determination of the sign and the magnitude of the change of mass which results when a positive and a negative electron are brought extremely close together.



Lorentz¹ speaks of this problem, but does not solve it either with respect to the sign or the magnitude of the effect. He does state, however, that if the electrons were to be brought into immediate contact, the total energy could not be found by addition, which may be considered as equivalent to the statement that the mass of a system made up in this way would not be the same as the sum of the masses of its parts. The fundamental equations used here as the basis of the calculation which follows, have been taken from the work of Lorentz.

The value of e , the charge on the electron, may be defined as

$$e = \iiint \rho d\tau,$$

where ρ is the volume density of the electricity, and $d\tau$ is an element of volume. For the purposes of the first part of the calculation, the electron may be considered as a point charge, but the values of the electromagnetic mass used later are given for the Lorentz form of electron, which takes the form of an oblate spheroid when in motion.

The space surrounding an electron must be considered as different from a space not adjacent to an electrical charge. If a charged particle is brought into this space it is acted upon by a force which varies from point to point, and has at every point in space a definite value and direction. This force is designated by \mathbf{E} , and is a vector point function. If the electron is in motion it acts as an electric current equal to $e\mathbf{u}$, where \mathbf{u} represents its velocity. The magnetic force due to this motion is easily seen to be a function of the current equivalent of the moving electron, and is also a vector, designated by \mathbf{H} . Then

$$\mathbf{H} = f(\mathbf{E}, \mathbf{u}, \phi)$$

¹ H. A. Lorentz, "The Theory of Electrons," 1909, pp. 47 and 48.

where ϕ is the angle between \mathbf{E} and the direction of motion. The direction of \mathbf{H} is perpendicular to the direction of \mathbf{u} and is at the same time circular.

It is evident that the total energy of the system is a function of both the electric and the magnetic intensities. For the purposes of this calculation the mass of a system is considered as electromagnetic, and hence as a function of the energy of the system. Therefore it is necessary to use some function of both \mathbf{E} and \mathbf{H} . This function is designated by \mathbf{G} and is called the electromagnetic momentum. The derivation of the equations for \mathbf{G} has been given by Lorentz, so here it will be sufficient to define it as

$$\mathbf{G} = [\mathbf{E} \mathbf{H}]/c$$

where $[\mathbf{E} \mathbf{H}]$ means the vector product of \mathbf{E} and \mathbf{H} , and c is the velocity of light. From the expressions obtained for \mathbf{G} it is easy to obtain those which represent the mass.

In the treatment which follows, only the longitudinal electromagnetic mass is considered, and terms containing u to a higher power than the first are disregarded, as they appear to be unimportant. The following general treatment, in which Heaviside units are used, gives an outline of the method:

For the field due to a system of charges

$$\frac{[\mathbf{E} \mathbf{H}]}{c} = \frac{[(\sum_i \mathbf{E}_i)(\sum_j \mathbf{H}_j)]}{c} = \frac{\sum_i [\mathbf{E}_i \mathbf{H}_i]}{c} + \frac{\sum_{(ij)} [\mathbf{E}_i \mathbf{H}_j]}{c}$$

where the summation $\sum_{(ij)}$ is the vector product of each i with each j . The first summation gives the electromagnetic momentum which would be due to the particles if their fields did not overlap, and the second term, which is the important one here, gives the effect of the overlapping of the fields. This may be called the "mutual electromagnetic momentum" and designated by $\bar{\mathbf{G}}$.

For point charges

$$\mathbf{E}_1 = \frac{(1 - u^2)e_1}{4\pi r^2(1 - u^2 \sin^2 \theta_1)^{3/2}}$$

at the point P_x, y, z . Let

$$(1 - u^2 \sin^2 \theta_1) = \beta_1^2$$

and

$$(1 - u^2) = k^2.$$

The transverse component of \mathbf{E} due to the two particles 1 and 2 is

$$\mathbf{E}_t = \frac{k^2 e}{4\pi} \left\{ \frac{\sin \theta_2}{\gamma_1^2 \beta_1^3} \pm \frac{\sin \theta_1}{\gamma_2^2 \beta_2^3} \right\}$$

where the sign is *positive* if the charges have the same sign, and *negative* if they are of opposite sign. As only the longitudinal component of the vector \mathbf{G} is desired, only the transverse component of \mathbf{E} is needed.

$$\mathbf{H} = u/c \mathbf{E} \sin \phi$$

where ϕ = the angle between \mathbf{E} and the direction of u . If \mathbf{E}_i is used, $\phi = 90^\circ$. Therefore

$$\mathbf{H} = u/c (\mathbf{E}_1 \sin \theta_1 \pm \mathbf{E}_2 \sin \theta_2)$$

$$\mathbf{G}_L = \frac{[\mathbf{E}, \mathbf{H}]}{c} = \frac{u}{c^2} (\mathbf{E}_1 \sin \theta_1 \pm \mathbf{E}_2 \sin \theta_2)(\mathbf{E}_1 \sin \theta_1 \pm \mathbf{E}_2 \sin \theta_2).$$

And

$$\begin{aligned} \bar{\mathbf{G}} &= \pm \frac{2u}{c^2} \int \mathbf{E}_1 \mathbf{E}_2 \sin \theta_1 \sin \theta_2 d\tau \\ &= \pm \frac{2u}{c^2} \frac{k^4 e^2}{(4\pi)^2} \int \frac{\sin \theta_1 \sin \theta_2}{\gamma_1^2 \gamma_2^2 \beta_1^3 \beta_2^3} d\tau. \end{aligned}$$

Now

$$\gamma^2 \beta^2 = \gamma^2 - u^2 (\gamma^2 \sin^2 \theta) \quad \text{and} \quad (\gamma^2 \sin^2 \theta) = \gamma^2.$$

Neglect all of the terms in u^2 .

$$d\tau = 2\pi y dy dx.$$

Then

$$\bar{\mathbf{G}} = \frac{uk^4 e^2}{8c^2 \pi^2} \cdot 2(2\pi) \int_0^\infty \int_0^\infty \frac{y^3 dy dx}{\sqrt{\{[(x-a)^2 + y^2][(x+a)^2 + y^2]\}^3}}$$

which is obtained by making use of the symmetry of the equation. Or

$$\begin{aligned} \bar{\mathbf{G}} &= \left(\frac{uk^4 e^2}{8c^2 \pi^2} \cdot 4\pi \right) \frac{1}{a} \int_0^\infty \int_0^\infty \frac{y^3 dx dy}{\sqrt{\{[(x-1)^2 + y^2][(x+1)^2 + y^2]\}^3}} \\ &= \frac{uk^4 e^2}{2\pi c^2 a} J \end{aligned}$$

where

$$\begin{aligned} J &= \int_0^\infty \int_0^\infty \frac{y^3 dx dy}{\sqrt{\{[(x-1)^2 + y^2][(x+1)^2 + y^2]\}^3}} \\ J &= \frac{1}{2} \int_0^\infty dx \int_0^\infty \frac{u du}{[(\alpha + u)(\beta + u)]^{3/2}}, \end{aligned}$$

where $u = y^2$.

$$\alpha = (x-1)^2; \quad \beta = (x+1)^2; \quad \alpha - \beta = (-4x).$$

$$\begin{aligned} J &= \frac{1}{2} \int_0^\infty dx \left[\frac{2[(\alpha + \beta)u + 2\alpha\beta]}{(\alpha - \beta)^3 [(\alpha + u)(\beta + u)]^{1/2}} \right]_0^\infty \\ &= \int_0^\infty \left[\frac{(\alpha + \beta)}{(\alpha - \beta)^2} - \frac{2\alpha\beta}{(\alpha - \beta)^2 \sqrt{\alpha\beta}} \right] dx \\ &= \int_0^\infty \frac{1}{16x^3} [\alpha + \beta - 2\sqrt{\alpha\beta}] dx \\ &= \int_0^\infty \frac{[\sqrt{\alpha} - \sqrt{\beta}]^2}{16x^3} dx \\ &= \int_0^\infty \frac{[(x-1) - (x+1)]^2}{16x^3} dx \end{aligned}$$

$$= \int_0^1 \frac{(-2x)^2}{16x^2} dx + \int_0^\infty \frac{(-2)^2}{16x^2} dx$$

$$\frac{1}{4} + \frac{1}{4}$$

$$\frac{1}{2}$$

$$G = \frac{uk^4}{4\pi ac^2}$$

The mass represented by this value of \bar{G} is

$$\Delta m = \pm e^2/4\pi c^2 a.$$

Now the longitudinal mass, m_1 is

$$m_1 = e^2/6\pi c^2 R,$$

where R is the radius of the electron. By division

$$\Delta m/m_1 = 3R/2a,$$

where a is equal to one-half the distance apart of the electrons.

In the application of this last equation, R must be taken as the radius of the positive electron, since it is assumed that it is the seat of practically all of the mass of the atom. For a decrease of mass of 1% in this simple case the distance apart of the positive and negative electrons would be, according to the equation, 300 times the radius of the positive electron. In order to produce a decrease of mass equal¹ to the average decrease of weight found for the 21 elements given in Table II, or 0.77%, the distance apart of the two electrons as calculated, would be 400 times the radius of the positive electron. This, however, does not give the result for any actual case which is known, and in general the nucleus of an atom must be more complex than this. In a more complex nucleus it is possible that the positive and negative electrons need not come so close together in order to give the same decrease of mass. It is evident that the calculation cannot be applied to any special atom until the mass of the positive electron is determined. If, as Rutherford seems to think probable, the positive nucleus of the hydrogen atom is the positive electron, then the most probable composition of the helium nucleus would be four positive electrons to two which are negative, and it would not seem improbable that in such a system the effect upon the mass of the positive electrons might be greater than in the simpler case used for the calculation, which would mean simply that the positive and negative electrons need not be so close together to produce the same effect on the mass. Whether this is true or not could not be determined without a knowledge of the structure of the helium nucleus. If, as Nicholson assumes, the

¹ From the electromagnetic theory the velocity of high speed electrons also exerts a perceptible influence upon the mass, but the magnitude of this effect has not as yet been determined for the case of the electrons in an atom.

hydrogen nucleus is complex, the decrease of mass in the formation of one helium atom from four of hydrogen, would be due to the closer packing of the positive and negative electrons in the helium nucleus.

Earlier in the paper it has been shown that the fact that the atomic weights on the oxygen basis are much closer to whole numbers than those on the hydrogen basis, is explained by what has been called the packing effect, or the change of mass involved in the formation of heavier atoms from hydrogen. The average of the packing effects for the elements considered, is 0.77%. This is also the value of this effect for oxygen, which happens to have been chosen as the fundamental element in the determination of atomic weights. If the number representing atomic weight of hydrogen, 1.0078, is decreased by this percentage amount, it becomes 1.0000, which is the fundamental unit in atomic weight determinations. The atomic weights of the twenty-five fundamental elements listed in Table II, are found, on the whole, to be very nearly products of this unit by a whole number. While the numerical unit of measurement does not change, the actual unit of mass, the mass of the hydrogen nucleus, varies slightly from atom to atom, and this variation causes the slight deviation of the atomic weights from whole numbers.

The opposite of the system here proposed would be, to suppose that the values of the atomic weights are wholly the result of accident. On this basis the probability that the atomic weights fall as close to whole numbers as they do, may be calculated. In such calculations oxygen is omitted, since its atomic weight is fixed as a whole number, and hydrogen is not used, since its atom contains only one hydrogen nucleus.

The first calculation made was that of the probability that *each* of the atomic weights should be as close as it is to a whole number. The data used are those of Table II. The chance that the atomic weight of nitrogen should entirely, by accident, deviate from a whole number by only 0.01 of a unit was determined by dividing the unit into the 200 divisions corresponding to the assumed accuracy (Landolt-Börnstein-Meyerhoffer, Tabellen) of 0.005. The greatest possible deviation would then be 100 divisions, while the actual deviation of 0.01 unit corresponds to 2 divisions. The probability is then one-fiftieth. The chance that any number of independent events should all happen is the product of the separate probabilities of their each happening. The probability calculated in this way is 2×10^{-22} , or

$$\frac{2}{10,000 \text{ billion billion}},$$

which indicates that there is practically no chance that the atomic weights are entirely the result of accident.

Another probability, which seems to be of more value in connection with the present problem, is that the *sum* of the deviations shall not ex-

ceed the sum actually found. This is of the form known as De Moivre's problem, and the method was used by Laplace¹ in calculating the probability that the sum of the inclinations of the orbits of the ten planets to the ecliptic is not greater than the value found at that time, 0.914187 of a right angle. The result obtained was 1.1×10^{-7} . The problem is stated in the following way: An urn contains $n + 1$ balls marked, respectively, 0, 1, 2, 3, n ; a ball is drawn and replaced: required the probability that after i drawings the sum of the numbers drawn will be s . This probability is the coefficient of x^s in the expansion of

$$\frac{1}{(n+1)^i} (1-x^{n+1})^i (1-x)^{-i},$$

or the probability P is

$$P = \frac{1}{(n+1)^i} \left\{ \frac{i+s-1}{i-1} \frac{1}{s} - \frac{i}{1} \frac{i-1+s-n-1}{i-1} \frac{1}{s-n-1} + \frac{i(i-1)}{1.2} \frac{i-1+s-2n-2}{i-1} \frac{1}{s-2n-2} \dots \right\}.$$

In the case of the atomic weights P gives the probability that the sum of the deviations from whole numbers shall equal s , which is not what is desired. The result wanted is the probability that the sum of the errors shall be equal to or less than s , or the summation of the Ps from 0 to s .
Now

$$\sum_{s=0}^{s=s} \frac{i+s-1}{i-1} \frac{1}{s} = \frac{i+s}{i} \frac{1}{s}$$

So the desired probability, P' is:

$$P' = \sum_{s=0}^{s=s} \frac{1}{(n+1)^i} \left\{ \frac{i+s}{i} \frac{1}{s} - \frac{i}{1} \frac{i+s-n-1}{i-1} \frac{1}{s-n-1} + \frac{i(i-1)}{1.2} \frac{i+s-2n-2}{i-1} \frac{1}{s-2n-2} - \frac{i(i-1)(i-2)}{1.2.3} \frac{i+s-3n-3}{i-1} \frac{1}{s-2n-3} \dots \right\}.$$

In solving this problem all of the first twenty-seven elements have been used with the exception of hydrogen and oxygen, and these *should* be omitted for the reasons given above. The errors in the determined values have been taken as they are given in Table II. The atomic weights used in the calculation are as follows:

| | | | | | |
|---------|--------|---------|-------|---------|-------|
| He..... | 4.002 | Mg..... | 24.32 | Ca..... | 40.07 |
| Li..... | 6.94 | Al..... | 27.1 | Sc..... | 44.1 |
| Be..... | 9.1 | Si..... | 28.3 | Ti..... | 48.1 |
| B..... | 11.0 | P..... | 31.02 | V..... | 51.0 |
| C..... | 12.005 | S..... | 32.06 | Cr..... | 52.0 |
| N..... | 14.01 | Cl..... | 35.46 | Mn..... | 54.93 |
| F..... | 19.00 | A..... | 39.88 | Fe..... | 55.84 |
| Ne..... | 20.15 | K..... | 39.10 | Co..... | 58.97 |
| Na..... | 22.995 | | | | |

¹ Laplace, "Oeuvres VII, Theorie Analytique des Probabilites," pp. 257-62.

The average probable error as determined from Table I is 0.043 unit, which is equivalent to about 24 divisions for one unit, or 12 divisions for half a unit, which is the maximum possible deviation from a whole number. Since n is 12, $n + 1$ is taken as 13. The sum of the deviations from whole numbers is 2.342, which is equal to 56 of the divisions determined above, or $s = 56$. The number of elements, i , is 26. The probability calculated on this basis is 6.56×10^{-8} , or approximately

15,000,000

It has been assumed in this paper that the cause of the deviations of neon, magnesium, silicon, and chlorine, which are exceptional in giving positive deviations from the atomic weights on the hydrogen basis, must be different from that which gives the deviations of the other elements. The cause of the deviation of neon has been explained, but for the others it is unknown. In the calculations of the probabilities given above these elements have been included. It may be of interest to note that if these elements had been excluded the probability for the 21 remaining elements would have been found to be about

7 billion

It is an interesting coincidence that the probability above found for the 27 lighter elements is about 1×10^{-7} , while the probability determined by Laplace that the sum of the inclinations of the ten planets then known, to the ecliptic, should not be greater than the sum of the measured values, is almost the same, or 1.123×10^{-7} . In the second paper of this series it will be shown that the atomic weights not only approximate whole numbers, but that these whole numbers are in addition *certain* numbers which are determined by a special system, and which may be given accurately by an equation of the form

$$W = 2(n + n') + \frac{1}{2} + [(-1)^{n-1} \times \frac{1}{2}].$$

The probability that the atomic weights should come so close to these *special* whole numbers is much less than that calculated above, so that the words of Laplace may be applied to the system presented here, as well as to the one he himself gives. That the atoms are built up of units of weight very close to one, and that therefore this modified form of Prout's hypothesis holds, "est indiquée avec une probabilité bien supérieure à celle du plus grand nombre des faits historiques sur lesquels on ne se permet aucun doute."

The accepted atomic weights on the oxygen basis as now used are closer to whole numbers than those given by Ostwald in 1890.¹ Ostwald's numbers are all larger than the corresponding whole numbers, so the

¹ *Allgemeine Chemie*, 1, p. 126 (1890).

deviations were all positive. On the other hand, the present values show both positive and negative deviations. The fact that the small change of 0.77% from the oxygen to the hydrogen basis eliminates practically all of the tendency of the atomic weights to be near whole numbers, when as many as 27 elements are considered as in Table II, shows that the atomic weight of oxygen cannot be taken as very different from 16.00 without obscuring this relationship. Thus it has been shown that the probability that the atomic weights on the oxygen basis would come entirely by accident as close to whole numbers as they do, is 6.56×10^{-8} , or about

$$\frac{1}{15,000,000}.$$

A change of only 0.77% from the oxygen basis causes an enormous increase in the probability that the atomic weights obtained in this way could be as close to whole numbers as they are, entirely by accident. Thus the chance that the sum of the deviations should come out as equal to, or less than, the sum actually found, is 0.105, or

$$\frac{1}{10}.$$

As has been seen, there are 27 atomic weights distributed over 59 units of atomic weight. The greatest common divisor of the whole numbers corresponding to the atomic weights is one. The atomic weights are therefore such that numerically they seem to be built up from a unit of a mass of one, and the probability results seem to show that this unit of mass must be very close to 1.000, expressed to three decimal places. On the other hand, this unit of mass must be somewhat variable to give the atomic weights as they are, even although a part of the variation, in some cases, may be due to the inaccuracy with which the atomic weights are known. This leads either to the supposition (1) that the atoms are built up of some unknown elementary substance, of an atomic weight which is slightly variable, but is on the average extremely close to 1.000, and which does not in any case deviate very far from this value, or to the idea (2) which is presented in this paper, that the *nucleus* of a known element is the unit of structure. The atom of this known element has a mass which is close to that of the required unit, and it has been proved that the decrease of mass involved in the formation of a complex atom from hydrogen units is in accord with the electromagnetic theory. The adoption of the first hypothesis would involve much more complicated relations. It would necessitate the existence of another elementary substance with an atomic weight close to that of hydrogen, it would involve a cause for the increase of weight in the formation of some atoms, and a decrease in other cases, and it would also involve the existence of another unit to give the hydrogen atom.

In the second paper, which follows, still more evidence in favor of the theory that the other atoms are complex atoms built up from hydrogen units will be presented, and it will be shown that there is also an important secondary unit of structure.

The writers wish to thank Professor A. C. Lunn, of the Department of Mathematics, for outlining for them the mathematical analysis of the determination of the packing effect.

Summary.

1. The atomic weights of the first 27 elements, beginning with helium, are not multiples of the atomic weight of hydrogen by a whole number, as they would be if Prout's original hypothesis in its numerical form were true. This may be expressed by the statement that the atomic weights on the hydrogen basis are not whole numbers. However, when these atomic weights are examined critically it is found that they differ from the corresponding whole numbers by a nearly constant percentage difference, and that the deviation is negative in sign, with an average value of -0.77% .

2. This percentage difference has been called the packing effect, and it represents the decrease of weight, and presumably the decrease of mass, which must take place if the other atoms are complexes built up from hydrogen atoms. The regularity in this effect is very striking, the values for a number of the lighter atoms being as follows: He, -0.77 ; B, -0.77 ; C, -0.77 ; N, -0.70 ; O, -0.77 ; F, -0.77 ; and Na, -0.77% , while the average value for the first 27 elements is -0.77% .

3. The regularity of the packing effect gives an explanation of the well-known fact that the atomic weights on the oxygen basis are very close to whole numbers, while this is not true of the atomic weights on the hydrogen basis except in the case of the lightest elements from helium to oxygen. The atomic weight of hydrogen on the oxygen basis is 1.0078 . If this were decreased by the value of the packing effect of 0.77% , it would become a whole number, 1.000 . Then, if the other elements are built up from hydrogen atoms as units, all of the atoms which are formed with a packing effect of -0.77% , must have whole numbers for their atomic weights; thus the atomic weights of the elements listed in Section 2, above, must be whole numbers in six of the seven cases listed, He, B, C, O, F, and Na. The fixing of any one of these six atomic weights as whole numbers causes the other five to be whole numbers also. Thus the atomic weights referred to carbon as 12.00 would be the same as those referred to oxygen as 16.00 . A variation of the atomic weight of an element on the oxygen basis from a whole number indicates that the packing effect for that element does not have the average value.

4. Recent work has shown that the nucleus of an atom must be extremely minute. Thus Rutherford gives the upper limit for the radius

of the relatively large and complex gold atom as 3.4×10^{-12} cm., while Crehore, who proposes another theory of the structure of the atom, considers that none of the electrons have orbits of a greater radius than 10^{-12} cm. The high velocity with which the β -particles are shot out in radioactive transformations has been considered as evidence that these electrons must come from much closer to the center of the atom than the assumed radius of the atom. It therefore seems practically certain that the electrons and positively charged particles which make up the nucleus of a complex atom, are packed exceedingly closely together. As a result of this close packing, the electromagnetic fields of the charged particles must overlap to a considerable extent, which would mean that the mass of the atom ought not to be equal to the sum of the masses of the individual particles from which it is built.

5. The closeness to which a positive and a negative electron would have to approach to give a decrease of mass equal to 0.77%, or the average value of the packing effect, is found by calculation to be to a distance of 400 times the radius of the positive electron. This case does not correspond to any element actually known, for the simplest of the atoms considered, helium, may be supposed to have a nucleus built up from four hydrogen nuclei and two negative electrons. However, the magnitude of the effect seems to be of the order which would be expected.

6. The probability for the first 27 elements, that the sum of the deviations of the atomic weights (on the oxygen basis from whole numbers) should by accident be as small as it is, is found to be one chance in fifteen million. On the other hand, a change of only 0.77% from the oxygen basis to that of hydrogen gives one chance in ten that the atomic weights should be as close to whole numbers as they are.

The second paper on atomic structure, which follows this one, gives still more evidence that the complex atoms are built up from hydrogen atoms as units of structure.

CHICAGO, ILL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE STRUCTURE OF COMPLEX ATOMS. THE HYDROGEN-HELIUM SYSTEM.

[SECOND PAPER ON ATOMIC STRUCTURE.]

BY WILLIAM D. HARKINS AND ERNEST D. WILSON.

Received April 12, 1915.

In the preceding paper it has been shown that the atomic weight relations of the elements are such as to make it extremely probable that the atoms are complex structures built up from hydrogen atoms. It therefore becomes important to determine in what way the hydrogen atoms unite

together to make up the complex. Rutherford proved that the α -particles which are shot out in the disintegration of the radioactive elements, have a mass of four units,¹ and that they give ordinary helium gas when they escape through the walls of a thin glass capillary tube in which the emanation is stored.² Fajans,³ Soddy,⁴ Russell,⁵ von Hevesy,⁶ and Fleck,⁷ have found that, when a radioactive substance ejects an α -particle, the new substance has different properties, and a different valence from those of the parent material. The change is such that the new element lies two places to the left in the periodic table, and therefore has an atomic number which is two less than before the alpha disintegration. It has been found that uranium, for example, can lose eight α -particles in eight steps, and change into a form of lead. From this it is seen that the radioactive elements, which have high atomic weights, must, at least in part, be built up of α -particles, and therefore of helium atoms, with this difference, that while the α -particle is probably present as a whole in the complex atom, the nonnuclear electrons of the helium atom, undoubtedly rearrange themselves in the complex atom, so that the helium atoms as a *whole* do not preserve their identity.

Now that it has been proved that the atoms of high atomic weight are built up, in part at least, of helium atoms, the question arises as to whether the same relations hold for the lighter atoms which have not been found to give an appreciable alpha disintegration. If they do, then a change of two places to the right in the periodic table, which is more accurately expressed as an increase of two in the atomic number, should increase the atomic weight by the weight of one helium atom, or by the number four. Since a change of two in the atomic number should increase the atomic weight by four, according to this theory, the average increase in the atomic weight per atomic number should be two. From this it might be expected that the tenth element would have an atomic weight equal to 20, and the twentieth element, an atomic weight of 40. That this is actually the case is seen, for neon, the tenth element has an atomic weight of 20, and calcium, the twentieth element, has a weight of 40. In order to investigate the question more in detail, a start may be made with helium, of an atomic number 2 and a weight of 4. The element of

¹ *Phil. Mag.*, [6] 28, 552-72 (1914).

² Rutherford and Soddy, *Phil. Mag.*, 3, 582 (1902); 453 and 579 (1903); Ramsay and Soddy, *Nature*, p. 246 (1903); *Proc. Roy. Soc.*, 72, 204 (1903); 73, 346 (1904); Curie and Dewar, *Compt. rend.*, 138, 190 (1904); Debierne, *Ibid.*, 141, 383 (1905); Rutherford, *Phil. Mag.*, 17, 281 (1909).

³ *Physik. Z.*, 14, 131-6 (1913).

⁴ *Chem. News*, 107, 97 (1913), and *Jahrb. Radioakt.*, 10, 188 (1913).

⁵ *Ibid.*, 107, 49 (1913).

⁶ *Physik. Z.*, 14, 49 (1914).

⁷ Fleck, *Trans. Chem. Soc.*, 103, 381 and 1052 (1913).

an atomic number four, should be heavier by the weight 4, or its atomic weight should be equal to eight. Above this the elements, if built up according to this helium system would have the weights:

| Atomic number. | Atomic weight. | Group number. |
|----------------|----------------|---------------|
| 6 | 12 | 4 |
| 8 | 16 | 6 |
| 10 | 20 | 0 |
| 12 | 24 | 2 |
| 14 | 28 | 4 |
| 16 | 32 | 6 |

where each step is made by adding the weight of one helium atom. The equation which represents the idea that the atomic weights of the lighter elements, belonging to even numbered groups, change in the same way as the elements in a radioactive series (namely, by an amount equal to four for a change of two groups in the periodic table), is

$$W = 2n,$$

where W is the atomic weight and n is the atomic number.

If a similar system is supposed to hold for the odd numbered elements, then beginning with lithium of an atomic weight seven, and an atomic number three, the atomic weights according to the simple helium system would be:

| Atomic number. | Atomic weight. | Group. |
|----------------|----------------|--------|
| 3 | 7 | 1 |
| 5 | 11 | 3 |
| 7 | 15 | 5 |
| 9 | 19 | 7 |
| 11 | 23 | 1 |
| 13 | 27 | 3 |
| 15 | 31 | 5 |
| 17 | 35 | 7 |
| 19 | 39 | 1 |

It is thus seen that for the odd groups as well as the even, the increase in the atomic weight is just that predicted for the addition of one helium atom for each step of two atomic numbers. The even and odd numbered elements are thus seen to belong to two different series. A single equation for both of these series may be easily written by introducing a term which disappears when n is even, and is effective when n is odd. If W is the atomic weight,¹

¹ Although it was not known to the writers at the time when this paper was written, it was found on looking up the subject that Rydberg, in an extremely important paper published in 1896 (*Z. anorg. Chem.*, 14, 80) found from a study of atomic weight relations that the elements belong to two series corresponding to the two formulas $4n$ and $4n-1$, where n is a whole number. Thus from an empirical basis he derived the same relationships as are developed in this paper from an entirely different standpoint; that is by the application of the relations found between the elements in a single radioactive series to the elements of small atomic weight.

$$W = 2n + \{1/2 + [(-1)^{n-1} \times 1/2]\}.$$

In Table I the atomic weights calculated according to this equation are given for the elements up to and including cobalt.

TABLE I.—A COMPARISON OF THE CALCULATED AND THE DETERMINED VALUES OF THE ATOMIC WEIGHTS.¹

| Element. | n. | Calculated. | Detd. | Diff. | Probable error in detn. |
|----------|-------|-------------|-------|---------------|-------------------------|
| He..... | 2 | 4 | 4.0 | 0 | 0.01 |
| Li..... | 3 | 7 | 6.94 | +0.06 | 0.05 |
| Be..... | 4 | 8 | 9.1 | -1.1 (= 1H) | 0.05 |
| B..... | 5 | 11 | 11.0 | 0 | 0.05 |
| C..... | 6 | 12 | 12.00 | 0 | 0.005 |
| N..... | 7 | 15 | 14.01 | +0.99 (= 1H) | 0.005 |
| O..... | 18 | 16 | 16.00 | 0 | ... |
| F..... | 9 | 19 | 19.0 | 0 | 0.05 |
| Ne..... | 10 | 20 | 20.0 | 0 | ... |
| Na..... | 11 | 23 | 23.00 | 0 | 0.01 |
| Mg..... | 12 | 24 | 24.32 | -0.32 | 0.03 |
| Al..... | 13 | 27 | 27.1 | -0.1 | 0.1 |
| Si..... | 14 | 28 | 28.3 | -0.3 | 0.1 |
| P..... | 15 | 31 | 31.04 | -0.04 | 0.1 |
| S..... | 16 | 32 | 32.07 | -0.7 | 0.01 |
| Cl..... | 17 | 35 | 35.46 | -0.46 | 0.01 |
| A..... | 18 | 36 | 39.88 | -3.88 (= 1He) | 0.02 |
| K..... | 19 | 39 | 39.10 | -0.10 | 0.01 |
| Ca..... | 20 n' | 40 | 40.07 | -0.07 | 0.07 |
| Sc..... | 21 1 | 44.1 | 44.1 | -0.1 | 0.1 |
| Ti..... | 22 2 | 48 | 48.1 | -0.1 | 0.1 |
| V..... | 23 2 | 51 | 51.0 | 0 | 0.1 |
| Cr..... | 24 2 | 52 | 52.0 | 0 | 0.05 |
| Mn..... | 25 2 | 55 | 54.93 | +0.07 | 0.05 |
| Fe..... | 26 2 | 56 | 55.84 | +0.16 | 0.03 |
| Co..... | 27 2 | 59 | 58.97 | +0.03 | 0.02 |

It is interesting to note that of the 28 elements in this table, 13, or very nearly half, have atomic weights which are divisible by 4, and that of all of the possible multiples of 4, only two are missing, *i. e.*, 2×4 and 9×4 . Seemingly to make up for the omission of the 9×4 , the 10×4 occurs twice. This may be represented as follows:

| | |
|---|--|
| $1 \times 4 = \text{He}$ | $8 \times 4 = \text{S}$ |
| $2 \times 4 = \text{missing, but represented by}$ $(2 \times 4) + 1$ | $9 \times 4 = \text{missing, but replaced by}$ $10 \times 4 = \text{A}$ |
| $3 \times 4 = \text{C}$ | $10 \times 4 = \text{Ca}$ |
| $4 \times 4 = \text{O}$ | $11 \times 4 = \text{Sc}$ |
| $5 \times 4 = \text{Ne}$ | $12 \times 4 = \text{Ti}$ |
| $6 \times 4 = \text{Mg}$ | $13 \times 4 = \text{Cr}$ |
| $7 \times 4 = \text{Si}$ | $14 \times 4 = \text{Fe}$ |

Of the atomic weights given in the table only one is divisible by 2, which is at the same time not divisible by four. Seven, or one-fourth of

¹ For the final equation including n' see section 3 of the summary.

the atomic weights, are divisible by 3, though the threes are not evenly spaced like the fours; three are divisible by 5, and two of these, argon and calcium, have the same atomic weight. Five are divisible by 7, and two by 9, and every possible multiple of 16 appears. According to this the most important numbers are 4 and 3, which is in accord with the equation given for the atomic weights, 3 being an important secondary unit.

Of the twenty-six elements given in this table, it is found that the equation gives the atomic weights of nine, or more than a third, with no difference between the calculated and determined values, and for six other elements the difference is practically within the limits of error of the determinations. For the three elements, Be (+1.1), N (−0.99), and argon (−3.88), the differences in the first two cases are practically equal to the weight of a hydrogen atom, and for argon the difference, when allowance is made for a possible change of the packing effect, is the weight of a helium atom. The deviations of magnesium (0.32), silicon (0.3), and chlorine (0.46), are somewhat large, the largest deviations being that of chlorine, which is equal to 1.3% of its atomic weight. These deviations are also exceptional in that they are greater on the basis of oxygen as 16 than they are on the basis of hydrogen as 1.00.

If these six cases of deviation, three of which can be explained as due to a deviation in the number of hydrogen or helium units, are neglected, it is found that for the other twenty elements the equation gives the atomic weights with so great an accuracy that the average deviation is only 0.045 unit, which is practically equal to the average probable error in the experimentally determined values as given by Landolt-Börnstein.

It has been seen that for the first twenty elements the average increase in weight is 2.00, or exactly the same increase as is found for the uranium or the thorium radioactive series. For the heavier elements the increase is somewhat more rapid. The increments are tabulated in Table II.

TABLE II.—THE CHANGE IN THE ATOMIC WEIGHT WITH THE ATOMIC NUMBER.

| Change of atomic number. | Final element. | Atomic wt. | Average increment. |
|--------------------------|----------------|------------|--------------------|
| 0-10 | Ne | 20 | 2.0 |
| 10-20 | Ca | 40.07 | 2.007 |
| 20-30 | Zn | 65.37 | 2.53 |
| 30-40 | Zr | 90.6 | 2.53 |
| 40-50 | Sn | 119.0 | 2.84 |
| 50-60 | Nd | 144.3 | 2.53 |
| 60-70 | Yb | 172.0 | 2.52 |
| 70-79 | Au | 197.2 | 2.80 |
| 79-92 | U | 238.5 | 3.20 |

The table shows that the increment 2.00 occurs twice, and 2.52 four times in the table. The increment in general increases with the atomic number.

As has been stated, if the first nine elements are considered, the aver-

age deviation of the atomic weights ($O = 16$) from whole numbers is only 0.019 unit, which is an extremely small deviation. If the last ten elements in Table I of the preceding paper are taken, it is found that the deviation, though much larger, is still small, and is equal to 0.075 unit. The last of these ten elements is cobalt, the second element in the eighth group for the first occurrence of the eighth group in the periodic table. Table III shows that at this point the deviation suddenly jumps to a relatively large value, being 0.32 for nickel, 0.43 for copper, and 0.37 for zinc, with an average of 0.247 for the ten elements beginning with nickel and ending with rubidium. The average deviation for the next ten elements, beginning with strontium and ending with cadmium, is also 0.247 unit, for the ten from indium to cerium it is 0.199, and for the

TABLE III.—DEVIATIONS OF THE ATOMIC WEIGHTS FROM WHOLE NUMBERS, SHOWING THAT FOR THE HEAVIER ELEMENTS THERE IS NO TENDENCY FOR THESE WEIGHTS TO APPROXIMATE WHOLE NUMBERS.

| Heavier elements. | | | | | | | | Lighter elements. ¹ | | |
|-------------------|---------|----------------------|---------------------------|----------------|---------|----------------------|---------------------------|--------------------------------|---------|----------------------|
| Element. | At. wt. | Diff. from whole no. | Probable error in at. wt. | Element. | At. wt. | Diff. from whole no. | Probable error in at. wt. | Element. | At. wt. | Diff. from whole no. |
| Ni.... | 58.68 | 0.32 | 0.02 | In.... | 114.8 | 0.2 | 0.5 | He.... | 4.00 | 0.00 |
| Cu.... | 63.57 | 0.43 | 0.05 | Sn.... | 119.0 | 0.0 | 0.5 | Li.... | 6.94 | 0.06 |
| Zn.... | 65.37 | 0.37 | 0.05 | Sb.... | 120.2 | 0.2 | 0.3 | Be.... | 9.1 | 0.10 |
| Ga.... | 69.9 | 0.10 | 0.5 | Te.... | 127.5 | 0.5 | 0.2 | B.... | 11.0 | 0.00 |
| Ge.... | 72.5 | 0.50 | 0.5 | I.... | 126.92 | 0.08 | 0.03 | C.... | 12.00 | 0.00 |
| As.... | 74.96 | 0.04 | 0.05 | Xe.... | 130.2 | 0.2 | 0.2 | N.... | 14.01 | 0.01 |
| Se.... | 79.2 | 0.20 | 0.1 | Cs.... | 132.81 | 0.19 | 0.05 | F.... | 19.00 | 0.00 |
| Br.... | 79.92 | 0.08 | 0.1 | Ba.... | 137.37 | 0.37 | 0.03 | | | |
| Kr.... | 82.92 | 0.08 | 0.1 | La.... | 139.0 | 0.0 | 0.3 | Av. variation, | | 0.024 |
| Rb.... | 85.45 | 0.45 | 0.05 | Ce.... | 140.25 | 0.25 | 0.1 | | | |
| Av. variation, | | 0.247 | | Av. variation, | | 0.199 | | Na.... | 23.00 | 0.00 |
| | | | | | | | | Al.... | 27.10 | 0.10 |
| Sr.... | 87.63 | 0.37 | 0.03 | Ta.... | 181.5 | 0.5 | 1.0 | P.... | 31.02 | 0.02 |
| Y.... | 89.0 | 0.0 | 0.2 | W.... | 184.0 | 0.0 | 0.5 | S.... | 32.07 | 0.07 |
| Zr.... | 90.6 | 0.4 | 0.2 | Os.... | 190.9 | 0.1 | 0.4 | Av. variation, | | 0.047 |
| Cb.... | 93.5 | 0.5 | | Ir.... | 193.1 | 0.1 | 0.2 | | | |
| Mo.... | 96.0 | 0.0 | 0.1 | Pt.... | 195.2 | 0.2 | 0.1 | Ar.... | 39.88 | 0.12 |
| Ru.... | 101.7 | 0.3 | 0.1 | Au.... | 197.2 | 0.2 | 0.1 | K.... | 39.10 | 0.10 |
| Rh.... | 102.9 | 0.1 | 0.05 | Hg.... | 200.6 | 0.6 | 0.4 | Ca.... | 40.07 | 0.07 |
| Pd.... | 106.7 | 0.3 | 0.1 | Tl.... | 204.0 | 0.0 | 0.2 | Ti.... | 48.10 | 0.10 |
| Ag.... | 107.88 | 0.12 | 0.02 | Pb.... | 207.1 | 0.1 | 0.1 | V.... | 51.00 | 0.00 |
| Cd.... | 112.4 | 0.4 | 0.03 | Ra.... | 226.4 | 0.4 | 0.3 | Cr.... | 52.00 | 0.00 |
| Av. variation, | | 0.247 | | Th.... | 232.4 | 0.4 | 0.5 | Mn.... | 54.93 | 0.07 |
| | | | | U.... | 238.5 | 0.5 | 0.5 | Fe.... | 55.84 | 0.16 |
| | | | | Av. variation, | | 0.260 | | Co.... | 58.97 | 0.03 |
| | | | | | | | | Av. variation, | | 0.072 |

¹ For a complete table of the lighter elements see Table II of the preceding paper.

twelve elements from tantalum to uranium, it is 0.260 unit. However, the value of Table II, as it stands, is very slight on account of the large probable errors in many of the atomic weights. This can be remedied by the choice of only such elements from the table as have accurately determined atomic weights. If thirteen elements are thus chosen as follows: nickel, copper, zinc, arsenic, bromine, rubidium, strontium, rhodium, silver, cadmium, iodine, caesium, and barium, the average deviation is 0.248 unit, while the theoretical deviation calculated on the basis that the atomic weights show no tendency to be near whole or any other special numbers, is 0.250 unit. Therefore, the tendency for the atomic weights to approximate whole numbers, which is very marked for the elements from helium up to an atomic weight of 59 (cobalt), seems to altogether disappear at the atomic weight 59 (beginning with nickel) and is not found for any of the elements which have an atomic weight higher than this value.

The reason for this abrupt change at the atomic weight 59, is not apparent. It may be in some unknown way connected with the first appearance at this point of new series, possibly formed by disintegration instead of aggregation; to a change in the effect of packing, or, if atoms exist which are lighter than hydrogen, it might possibly be due to their inclusion. If the first suggestion is considered, it is found that when the elements of high atomic weight are reached several series are known to exist. Thus the isotopes of lead, lead from radium and radium B differ in atomic weight by eight units, the isotopes radium F and radium A differ by the same amount, and radio-thorium and uranium X_1 differ by six units. If the members of the actinium series could be included, some of these differences in the weights of one species of atom would be made even larger. Where such differences exist in the weights of the different atoms having a single atomic number, it cannot be expected that any very simple relations can be found to exist for atoms of a high atomic weight, except where it is possible to compare the weights of the members of a single series, such as the uranium-radium, the thorium, or the actinium radioactive series.

It is quite possible that these differences of series go downward in the periodic system to relatively low atomic weights. Thus Aston claims to have separated neon, with an atomic weight 20.2, into neon and meta-neon, the atomic weights for which have been found by Thomson to be 20 and 22, so that the deviation of neon from the law of the approximate whole number by the amount $+0.2$ is probably only an apparent one. It is of interest that the difference between the atomic weights of neon and meta-neon, as found by Thomson, is two, which is the same as the average increment in the weights of the lighter elements, and is equal to the average difference between the weights of isotopes in the radioactive

series. This average difference has been supposed to be also the actual difference between any two adjacent isotopes as listed below under any single atomic number:

Atomic number.

- 82. Lead from Ra, Lead from Th, Ra D, Th B, Ra B.
- 83. Bi, Ra E, Th C, Ra C.
- 84. Ra F, Th C, Ra C, Th A, Ra A.
- 86. Th Em, Ra Em (Nt).
- 88. Th X, Ra, Ms Th.
- 90. Ra Th, Io, Th, UX₁.

However, these assumed differences of two have depended upon the fact that the atomic weights used for uranium and thorium have been 238.5 and 232.4, or a difference of practically 4 plus 2. The latest determination of the atomic weight of uranium by Hönigschmidt¹ gives a value of 238.18, which would not accord with this relationship for the individual differences. The difference between two isotopes belonging to a single radioactive series is, however, not affected by this result, and may still be assumed as four. However, in radioactive changes where a helium atom is lost, the new atom which is formed is not exactly four units lighter than the parent atom, since the packing effect varies with the change. How this effect varies in these heavy atoms cannot be told from the data now available, since the accuracy of the atomic weight determinations is not sufficient for this purpose, but the variation may be calculated approximately from the heat evolved in all cases where the heat change can be determined. It is of course self-evident that for deductions in regard to such atomic weight relations, the percentage accuracy must be much greater than is necessary for the study of the lighter elements. The difference between Hönigschmidt's values for uranium and for radium² (at. wt. = 225.97) is 12.21, or 0.21 more than the weight of three helium atoms.

Now that certain elements have been found to exist in isotopic forms, it becomes apparent that still other elements may do the same in cases which have not been recognized, so that in dealing with any single species of element it is uncertain whether this is an individual with respect to its atomic weight. The great regularity with which the elements follow the relationships given in these papers, up to an atomic weight of 59, suggests that with the exception of the cases of neon, silicon, magnesium, and chlorine, isotopes probably do not exist to any large extent for any of these elements, if they exist at all. There is still another possibility which suggests itself, and that is that the different atoms of a single atomic species differ in weight among themselves, and that the atomic weights as found are simply statistical averages. If this were true, the constancy

¹ *Z. Electrochem.*, 20, 449 (1914).

² *Sitzungsb. kais. Akad. Wien.*, 121, Abt. IIA, 1973 (1912); *Monatsh.*, 34, 283 (1913).

of the results obtained in atomic weight determinations which after all is not of an extremely high order, would be due to the fact that in a single determination such an enormous number of atoms is used. For example, if in one determination the weight of silver chloride obtained were 7.16 g., the number of chlorine or silver atoms in the precipitate would be 3×10^{23} , or thirty thousand billion billion. The statement of the above idea is not meant to be understood as an advocacy of such a theory, but only to point out the possibility that such might be the case.

TABLE IV.—A SYMBOLICAL REPRESENTATION OF THE ATOMIC WEIGHTS OF THE ELEMENTS IN THE FIRST THREE SERIES OF THE PERIODIC TABLE.

H = 1.0078.

| | He He | Li He+H ₂ | Be 2He+H | B 2He+H ₂ | C 3He | N 3He+H ₂ | 6. O 4He | 7. F 4He+H ₂ | | |
|---------|------------|--------------------------|-------------|--------------------------|------------|--------------------------|----------------|-------------------------------|------------|---------------------------|
| Ser. 2. | | | | | | | | | | |
| Theor. | 4.00 | 7.00 | 9.0 | 11.0 | 12.00 | 14.00 | 16.00 | 19.00 | | |
| Det .. | 4.00 | 6.94 | 9.1 | 11.0 | 12.00 | 14.01 | 16.00 | 19.00 | | |
| | Ne 5He | Na 5He+H ₂ | Mg 6He | Al 6He+H ₂ | Si 7He | P 7He+H ₂ | S 8He | Cl 8He+H ₂ | | |
| Ser. 3. | | | | | | | | | | |
| Theor. | 20.0 | 23.00 | 24.00 | 27.0 | 28.0 | 31.00 | 32.00 | 35.00 | | |
| Det .. | 20.0 | 23.00 | 24.32 | 27.1 | 28.3 | 31.02 | 32.07 | 35.46 | | |
| | Ar 10He | K 9He+H ₂ | Ca 10He | Sc 11He | Ti 12He | V 12He+H ₂ | Cr 13He | Mn 13He+H ₂ | Fe 14He | Co 14He+H ₂ |
| Ser. 4. | | | | | | | | | | |
| Theor. | 40.0 | 39.00 | 40.00 | 44.0 | 48.0 | 51.0 | 52.0 | 55.00 | 56.00 | 59.00 |
| Det .. | 39.9 | 39.10 | 40.07 | 44.1 | 48.1 | 51.0 | 52.0 | 54.93 | 55.84 | 58.97 |

Increment from Series 2 to Series 3 = 4He

Increment from Series 3 to Series 4 = 5He (4He for K and Ca)

Increment from Series 4 to Series 5 = 6He

Table IV gives Series 2, 3 and 4 of the periodic system, built up by adding the weight of one helium atom for each change of two places to the right, and by adding enough multiples of the weight of a hydrogen atom to make up the atomic weight. In order to make the relationship apparent a symbolical representation has been used, He being taken to stand for the weight 4, and H for the weight 1.00. Built up in this way, the atomic weights of all of the members of the even numbered groups (with the exception of beryllium) may be represented by a whole number of symbols He, while all of the atomic weights in the odd groups may be represented by 3H plus a whole number of symbols He.

In the fourth, or argon series, the atomic weights begin to increase more rapidly than in the second and third series. This effect is first seen in the case of argon, which with a calculated atomic weight of 36, has instead a weight of practically forty, or too much by the weight of one helium atom. This effect dies out in potassium and calcium, and then appears again in scandium, titanium and the other members of this series. It becomes apparent in another way on studying the increment of weight in passing from a member of one series to the corresponding member

of the series below it. Thus the second member in each group is obtained from the first by adding 4He. In going from the second to the third member of the group the increase is the same (4He) to give potassium or calcium, but is 5He to give argon, titanium, vanadium, chromium, and manganese.¹ This in a sense explains how the atomic weight of argon comes to be greater than that of potassium, and practically equal to that of calcium. In going from the third to the fourth member of each group, it is necessary to add 6He, but the increase in this case seems to be due to the interposition of the eighth group elements, iron, cobalt, and nickel.

While both the law of the approximate whole number, and the hydrogen-helium system here presented, become suddenly much less accurate beginning with the element nickel, this does not necessarily mean that the hydrogen-helium system breaks down at this point, since there are several possible causes, already mentioned, which may account for the sudden increase in the deviations. The eighth group fills the position of a transition group between the seventh group and the first, which shows that it fills exactly the place of the zero group in the other series. The first member of the eighth group tried thus has an even number as its atomic number. The second member has an odd, and the third an even number, which gives to the first group an odd atomic number. This is entirely in accord with the system, which would fail at this point if there had been two instead of three members in each position in the eighth group.

According to the rule that the atomic weights of the elements increase alternately by 3 and by 1, then since iron has a weight of 56, that of cobalt should be 59 (detd. = 58.97), nickel should be 60 (detd. = 58.68), and copper 63 (detd. = 63.57). The first large negative deviation among the elements of even atomic numbers, of any of the actual atomic weights from the theoretical value, is thus found for the element nickel. Now it has been found that if it is studied from the standpoint of its behavior toward X-rays, nickel behaves as an element of a considerably higher atomic weight than the determined value. The wave lengths of the strong K radiations as found by Moseley are proportional to the reciprocals of the squares of the atomic weights. If cobalt is taken as a standard of reference (the square of the atomic weight and wave length being taken as 100 for this element), the values, part of which were calculated by Kaye,² come out as follows:³

¹ In comparison with the other members of the same series it is potassium and calcium rather than argon, which are exceptional.

² "X-Rays," 200.

³ This table could be extended by including the values of the nuclear charge, when it would be seen that the wave lengths seem to be determined by the nuclear charge as found by Moseley, rather than by the atomic weight.

| | Al. | Si. | Cl. | K. | Ca. | Ti. | V. | Cr. | Mn. |
|-----------------------|------|------|------|-----|-----|-----|-----|-----|-----|
| (Atomic weight) | 21.1 | 23.0 | 36.1 | 44 | 46 | 66 | 75 | 78 | 86 |
| 1/Wave length..... | 21.5 | 25.2 | 37.8 | 47 | 53 | 65 | 72 | 78 | 85 |
| | Fe. | Co. | Ni. | Cu. | Zn. | Rh. | Pd. | Ag. | |
| (Atomic weight)..... | 90 | 100 | 99 | 116 | 123 | 304 | 328 | 334 | |
| 1/Wave length..... | 92 | 100 | 108 | 116 | 124 | 298 | 314 | 321 | |

The atomic weight of nickel, if calculated from the value 108 as given in this table, comes out as about 61.2, while the other elements from titanium up to and including rhodium, give a very close agreement. The principle as given above is derived from Whiddington's result that the energy of a characteristic X-ray is roughly proportional to the atomic weight, and from the quantum theory of radiation, according to which the energy of a radiation is inversely proportional to its wave length.

A study of the packing effects, as given in Table II of the preceding paper, shows that where an atom is built up entirely of helium atoms, then, on the average, the decrease in mass is practically due entirely to the primary formation of the helium atoms, and not at all to the aggregation of these into atoms which are heavier. From this point of view an atom composed entirely of helium units would have extreme instability in so far as its disintegration into helium units, in *comparison* with its instability with reference to a hydrogen decomposition. Such an atom in a radioactive transformation should lose α -particles much more readily than hydrogen nuclei, in fact, if it is remembered that the alpha decomposition is itself not complete in any case, it will be seen that it is doubtful if such an atom would ever give a detectable hydrogen disintegration.

If the atoms are built up entirely according to the special system presented in Table IV, according to which the members of even numbered groups are in general aggregates of helium alone, then since all of the radioactive elements which are now known to give a simple alpha decomposition (that is without an accompanying beta change) belong to even numbered groups, they could not be expected to give hydrogen upon disintegration. Thus one of the chief objections to the theory that the atoms are hydrogen complexes, which is based on the fact that up to the present time no hydrogen has been detected as the product of any radioactive change, is seen to be not contrary to, but rather in accord with, the theory as presented in these papers. The exceptional case of beryllium shows, however, that even numbers of even numbered groups sometimes contain a hydrogen nucleus which was not contained in one of the helium nuclei from which the atom was built, so that there still remains the possibility, though the probability seems small, that hydrogen nuclei might be liberated from atoms belonging to these groups. There is no evidence that the particular system presented in Table IV holds exactly for the atoms of high atomic weight, but the general form of the system indicates at least that the atoms contain more helium than independent

hydrogen units, and this seems in accord with the fact that uranium loses α -particles in eight steps, and is changed into a form of lead, without any apparent loss of a hydrogen nucleus.

The stability with which the hydrogen nuclei which are not contained in helium groups, but which generally occur in threes (H_3 in Table II), are built into the complex atoms, is not indicated with any degree of accuracy, but in the case of lithium it seems to be great, for lithium shows the extremely large packing effect equal to 1.57%, which might seem doubtful but for the care taken by Richards and Willard¹ in the determination of this atomic weight.

The hydrogen-helium system here presented is entirely in accord with, but independent of, the astronomical theory that the order in which the elements appear in the stars is first nebulium, hydrogen and helium, then such of the lighter elements as calcium, magnesium, oxygen, and nitrogen, and finally iron, and the other heavy metals, although in the present system it has not been found necessary to include nebulium. Some of the nebulae give bright line spectra of nebulium, hydrogen and helium, such Orion stars as those of the Trapezium give lines for hydrogen and helium, while those that are more developed show magnesium, silicon, oxygen and nitrogen, and some of the other low atomic weight elements in addition. Bluish white stars such as Sirius give narrow and faint lines for iron, sodium, and magnesium, and the solar stars give much weaker hydrogen spectrum, and many more and stronger lines for iron and the heavy metals. The astronomical theory that the heavier elements are thus formed from those of smaller atomic weight is of extreme interest, but the evidence for it is somewhat uncertain, since it is possible that it is the difference in the density of the different elements which is the effective factor in causing the spectra to appear in the order in which they are found to occur. The relative brightness of the different lines also varies greatly, such lines as the calcium H and K lines being extremely strong, and this also interferes with the determination of the order of the appearance of the elements in the stars. On the other hand, the evidence presented in these papers, which seems to show that the elements are atomic compounds of hydrogen and helium, appears to give some support to the theory of the evolution of the heavier atoms from those which are lighter. The evidence for the hydrogen-helium system is, however, very much stronger and more complete than that for the evolution of the elements in the stars.

Summary.

1. The fundamental idea of this, the second paper on atomic structure, is to show that the system which has been found to apply to the atomic weight and valence relations of the members of each of the radio-

¹ Richards and Willard, *THIS JOURNAL*, 32, 4 (1910).

active series, also holds true for the lighter atoms. In a radioactive series it is found that a loss of an α -particle with a mass of four decreases the valence by two, and thus shifts the element two groups to the left in the periodic table, and decreases the atomic number by two. If this is true for the lighter elements, beginning with helium, then the addition of the weight of a helium atom for each increase of two in the atomic number ought to give the atomic weights of the elements belonging to the even numbered groups. The atomic weights found by this method are the same on the whole as the determined values, which shows that the theory accords with the facts.

2. The lithium atom, which is the first atom in the odd numbered group, is heavier than the helium atom by the weight of three hydrogen atoms. It would be very remarkable if the atoms of odd atomic number follow the same rule as those of even atomic number, but that they do is indicated by Table IV, which shows that for the odd numbered groups as well, each increase of two in the atomic number results in an increase of four in the atomic weight.

3. The atomic weights of the lighter elements are given with considerable accuracy by the equation

$$W = 2n + (1/2 + 1/2 (-1)^{n-1}),$$

where W is the atomic weight and n the atomic number. In the case of the heavier elements another term enters, so that the more general equation may be given:

$$W = 2(n + n') + [1/2 + 1/2 (-1)^{n-1}]$$

4. Of the 27 elements from helium to cobalt, 13, or nearly one-half, have atomic weights divisible by four, and these elements in general belong to even numbered groups in the periodic table. Of all the possible multiples of four only two are missing, *i. e.*, 2×4 and 9×4 , and seemingly to make up for the omission of the 9×4 , the 10×4 occurs twice. An explanation of the omission of the 2×4 and its occurrence as $(2 \times 4) + 1$ will be given in a later paper.

5. If the atomic weights increase by the weight of one helium atom for an increase of two in the atomic number, the average increase in the atomic weight per atomic number should be 2. That this is in accord with the facts is shown, for neon with an atomic number 10 has an atomic weight of 10×2 or 20, and calcium, with an atomic number 20, has an atomic weight equal to 20×2 or 40.

6. According to the first paper, the magnitude of the packing effect for helium is 0.77%, which is the same as the average of the packing effects for the first 27 elements, so that if a more complex atom is built of helium groups alone, then in general nearly all of the packing effect is due to the primary formation of the helium nucleus from four hydrogen

nuclei and two negative electrons, and almost no packing effect results from the aggregation of these helium nuclei into more complex atoms. On this view the helium nuclei must be very greatly more stable than the nuclei of the more complex atoms which they form, so that such an atom, made up entirely from helium units, should give helium and not hydrogen by its primary decomposition. This is in accord with the behavior of the radioactive elements when they disintegrate. It is of interest to note that the members of the radioactive series which are now known to give helium on decomposition, belong to the even numbered groups on the periodic table, and therefore to those groups which are shown in Table IV, as helium aggregates alone. That these heavy atoms must contain a considerable number of helium units is shown by the fact that uranium changes into lead by eight steps in which it loses α -particles.

7. The hydrogen-helium system gives an explanation of the fact that argon has an atomic weight of 40, which is higher than that of potassium, which has an atomic number higher by 1. A study of Table IV makes the reason apparent, and shows that in *comparison* with other members of Series 4 in the periodic table, it is potassium and calcium, and not argon, which are exceptional. In comparison with the members of Series 3, and potassium and calcium, it is of course the argon which is exceptional. As the atoms grow heavier there is a tendency to take on helium (or perhaps hydrogen) groups more rapidly than is the rule in the case of the lighter elements.

Later papers by one of the writers will consider the nuclear and non-nuclear electrons, and the relations of the periodic system to the hydrogen-helium system presented in this paper.

CHICAGO, ILL.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

RECENT WORK ON THE STRUCTURE OF THE ATOM.

[THIRD PAPER ON ATOMIC STRUCTURE.]

BY WILLIAM D. HARKINS AND ERNEST D. WILSON.

Received March 27, 1915.

When Dalton¹ advanced his atomic theory of the constitution of matter, he thought of the atom as the ultimate material unit. The discovery of the phenomena of radioactivity, however, made it evident that this view was incorrect, and showed that the atom must be complex. The question of its structure has remained unsolved for a long time, and it is only very recently that there has been any experimental work upon which to base a theory. In this paper practically all of the important

¹ "On Chemical Synthesis, from a New System of Chemical Philosophy," Manchester, 1808, pp. 211-6, 219-20.

recent work bearing on this subject will be considered, and, wherever possible, the results due to the different investigators combined. As the results often seem to be contradictory, the difficulty of reaching any definite conclusion is great.

One of the first difficulties which arises in the attempt to develop an "atom model" is the fact that even at the present time we know nothing of the nature of positive electricity. The different characteristics of the negative electron have been known for some time, but the question of a positive electron is still open.

The first atom model was suggested by Lord Kelvin,¹ and consisted of concentric rings of rotating negative electrons in a sphere of homogeneous positive electricity the size of the atom. This model has come to be known as the Thomson atom, due to the fact that he developed it quite completely, and worked out in detail the number of electrons in the various rings necessary to give stable systems. The advantages of this construction lie in the relative simplicity of the mathematical calculation of the distribution and velocities of the electrons, as compared with the great difficulties involved in a satisfactory solution of such problems in connection with the later atom models. Thomson has shown that such an atom imitates to a large extent the properties of our known chemical atoms and explains why some are electropositive, others electronegative, and the variation of the chemical properties with the atomic weight.

One objection to this model, which also applies to the other models unless a rather questionable assumption is made, is that the atoms so formed would not be stable, for according to the electromagnetic theory, electrons in orbital motion must radiate energy, and hence at some time the atom would break up.

An objection that is even more important is that the positive spheres of Kelvin would have an electromagnetic inertia which would be negligible compared with that of even a single negative electron, leaving practically all of the mass of the atom unaccounted for on this theory.

The first theory of the constitution of the atom with any experimental work as a basis is due to Rutherford. He made use of the phenomenon of the scattering of alpha and beta particles in passing through matter.² The deflection is more marked for the beta than for the alpha particle, due to the smaller momentum of the former. There seems to be no doubt that the particles pass through atoms, and that their deflections are due to the intense electric field within the atom. Calculation shows that the distribution of the positive electricity assumed in the Thomson atom does not admit of sufficiently strong fields to deflect an alpha particle through a large angle, and the scattering of the alpha and beta rays in passing through thin sheets of metal had been attributed to a number of small scatterings. Geiger and Marsden,³ working with gold foil

0.00004 cm. thick, found that about 1 in 20,000 alpha particles was deflected at an average angle of 90° . Also, Geiger⁴ showed by the theory of probabilities that the most probable deflection was 0.87° , and that the chance of a 90° deflection was vanishingly small. In the theory of the Thomson atom the large deflections were considered as due to the accumulative effect of a number of small ones. The distribution of alpha particles deflected through large angles does not follow the probability curve. Also, after one collision the probability of the same ray suffering another in such a way as to give a larger deflection is very small.

Considering the deflections as due to a single encounter with an atom, Rutherford has obtained an expression for dm , the fraction of the total number of alpha particles which are deviated between p and $p + dp$.

$$dm = \pi/4 \, ntb^2 (\cot \phi/2 \csc \phi/2) \, dp$$

where n is the number of atoms per unit volume, t the thickness of the metal, b the distance from the center to which an alpha particle would penetrate if shot directly at the atom, and p the perpendicular distance from the center of the atom to the extension of the line of path of the approaching alpha particle. Geiger⁵ has shown this equation to be true between 30° and 150° .

Thomson considered the scattering as due to the accumulative effect of a number of small scatterings, and obtained the following expressions: The average deflection, θ_t , for a sheet of thickness t is $\theta_t = 3\pi b/8 \sqrt{\pi nt}$. The probability p_1 that the deflection is greater than ϕ is $p_1 = e^{-\phi^2/\theta_t^2}$.

Rutherford shows that the probability p_2 for the same thing based on the theory of a single scattering is

$$p_2 = \frac{\pi}{4} b^2 nt \cot^2 \frac{\phi}{2}$$

If $p_2 = 0.5$, $p_1 = 0.24$. If $p_2 = 0.1$, $p_1 = 0.0004$.

Thus the probability on Rutherford's assumption is greater than that on Thomson's. Both of these theories are developed on the assumption that the forces between the particles are electrical, and follow the inverse square law. Darwin has shown that this is the only law of force which is consistent with the facts.*

These considerations would seem to indicate that the large deflections actually found must be due to a single encounter with an atom, and in order to obtain the necessary strength of field, the positive charge would have to be concentrated at a small point instead of being evenly distributed throughout the entire volume of the atom, as in the theory of Thom-

* NOTE.—A recent paper by Hicks takes into account the magnetic forces also, and shows that their effect may be of the same order of magnitude as that of the electrostatic forces only. Any theory which is complete must take account of both. Calculations based on only one would seem to be of doubtful reliability. See Hicks, *Phil. Mag.*, Jan., 1915.

son. The negative electrons vibrate around this positive nucleus, forming a kind of miniature solar system. This is the type of atom first suggested by Nagaoka.⁶ From the measured deflections, Rutherford estimated that the charge on the nucleus was approximately equal to one-half the atomic weight of the element times the electronic charge. The large deflections are due to the alpha particle passing very close to the nucleus.

With beta rays the effects are slightly different, for since the force is attractive they increase speed on approaching the atom. By ordinary electrodynamics this involves a loss of energy by radiation, and an increase in apparent mass. Darwin showed that if the beta particle passed very close to the nucleus it would describe a spiral, and eventually fall in. This might explain the disappearance of swift beta particles in their passage through matter.

The case of the passage of the alpha particles through hydrogen is of particular interest,⁷ for, since the alpha particle is heavier than the hydrogen atom, the recoil due to the close approach of the atom and the particle should be very large. It was shown that, as a result of a collision, the hydrogen atom should attain a velocity of 1.6 times, and hence a range of about four times that of the alpha particle itself. Marsden⁸ actually found hydrogen atoms with a range of about 90 cm. in hydrogen in which the alpha particles had a range of only 20 cm.

From the data on the scattering of the alpha rays in passing through a gold leaf, it is possible to calculate an upper limit for the radius of the nucleus of the gold atom.

Ne = charge on the nucleus (positive).

R = the radius of the sphere of electric action.

Ne = the value of the negative charge surrounding the nucleus.

x = electric force at a distance r from the center.

v = potential force at a distance r from center.

Then $x = Ne \left(\frac{1}{r^2} - \frac{r}{R^3} \right)$ and $v = Ne \left(\frac{1}{r} - \frac{3}{2R} + \frac{r}{2R^3} \right)$.

m = mass of alpha particle.

u = velocity of alpha particle.

E = charge on the alpha particle.

Let the alpha particle be shot directly at the atom, being brought to rest at a distance b from the center. Then

$$\frac{1}{2} mu^2 = NeE \left(\frac{1}{b} - \frac{3}{2R} + \frac{b^2}{2R^3} \right).$$

If N is assumed to be 100, which cannot be very far from the correct value for gold, the distance b for an alpha particle of velocity 2.09×10^9 cm. per second is found to be 3.4×10^{-12} cm. This gives a maximum value for the radius of the nucleus of the gold atom.

Darwin⁸ has made a similar calculation for the hydrogen atom and obtains the value 1.7×10^{-13} cm. for the diameter. This is smaller

than the diameter of the negative electron, which is ordinarily given as 2.0×10^{-13} cm. The question arises as to whether the mass of this positive nucleus is entirely electromagnetic, like that of the negative electron. The electrical mass of a charged body is $2e^2/3a$, where e is the charge, and a the radius. Using this formula the radius of the positive nucleus of hydrogen comes out to be $1/1830$ that of the negative electron. Rutherford⁹ suggests that it is probable that the hydrogen nucleus is the long sought positive electron.

Rutherford has shown that it is impossible to account for the high speed of expulsion of some of the alpha and beta particles if they come from a ring of atomic radius. They must come from a point very close to the center, which suggests that they are shot from the nucleus of the atom.

The present theory of the constitution of the atom is based on the facts given above. Each atom of matter is supposed to be made up of a positively charged nucleus around which rotate the negative electrons. In the heavier atoms there are negative electrons in the nucleus also. The nucleus is the seat of practically all of the mass of the atom, for the negative electrons contribute very little mass. Barkla,¹⁰ from his work on the passage of X-rays through matter, suggested that the charge on the nucleus is about $1/2 Ae$, where A is the atomic weight of the element. Vau den Broek,¹¹ and later Bohr,¹² suggested that the number of units of charge is Ne where N is the number of the element when the elements are arranged in order of increasing atomic weight, or what is now called the atomic number.

Moseley's¹³ work on the X-ray spectra of the elements is very important also, in helping to give an insight into the constitution of the atom. Working along the line first suggested by Laue,¹⁴ and Bragg;¹⁵ Moseley, and Darwin have developed an experimental method for determining the X-ray spectra of the elements by reflection from crystal surfaces. When an element is used as the anticathode in an X-ray tube, it emits a characteristic radiation of a frequency roughly 1000 times as great as that of the visible light waves. Each element is characterized by two different radiations which have been called the K radiation and the L radiation.¹⁶ The K radiation is composed of two lines which Moseley has called the α line and the β line. These are the ones used the most by him for purposes of calculation. The L radiation is not nearly as penetrating as the K radiation, and usually consists of about five lines.

Moseley recorded the spectra photographically, instead of using an electroscope for a detector as did Bragg, and he examined the X-ray spectra of the elements from aluminium to gold. He found a very remarkable relationship between the frequencies of the lines of the various elements. In going from one element to the next higher in atomic weight there was a shift of the two lines of the K series toward the violet. That is, there is

a change in the frequency of the spectrum lines with a change of the element. Moreover there is a very simple relationship between these frequencies. Thus considering the α line, the frequency is expressed by the formula

$$\nu = K(N - 1)^2$$

in which K is a constant, and N is a number which increases by one in passing from one element to the next higher in atomic weight. If 13 is chosen for the value of N for aluminium, and a corresponding value of K , N turns out to be the atomic number of the elements. Thus N determines the X-ray spectrum of any element. Moseley finds that between aluminium and gold the order of the elements according to N is the same as that of the atomic weights except where the latter would put the element out of place in the periodic table. Moseley finds only three unknown elements between aluminium and gold.

He has shown that neoytterbium and lutecium exist, but that Urbain's celtium is a mixture. According to his system thulium I and thulium II of Welsbach exist, but not thulium III. A homolog of Mn between Mo and Ru remains to be found as does another element between Os and W.

Moseley concludes that the number N is the charge on the nucleus of an atom, and that this charge increases one step at a time from one element to the next. According to this view it is perfectly possible to have two elements of very different atomic weight that have the same X-ray spectrum, providing only that they have the same nuclear charge.

Such elements would also be identical chemically, and so far as is known at the present time would have identical spark and arc spectra.

This seems to be borne out by the fact that Aston,¹⁷ working with J. J. Thomson, found two neons with atomic weights 20 and 22, which are otherwise identical, and have the same spectrum. He was only able to separate them by diffusion methods, which depend on the atomic weight and hence upon the density. Also Russell and Ross,¹⁸ and Exner and Haschek,¹⁹ working with a strong ionium solution, could not obtain any spectrum except that of thorium, of which ionium is an isotope.

This theory of the dependence of the chemical and physical properties of the elements on the nuclear charge is supported by recent work on the radioactive elements. The position of all these elements in the periodic table was an unsolved problem until it was shown that two or more elements could occupy the same place in the table. It has been supposed for some time that certain of the radio-elements were inseparable by any known chemical means. Fajans, Soddy, and others make this a general property of these elements, and treat each as the chemical analog of one or the other of the known elements. Two elements which occupy the same space in the periodic table and are inseparable by ordinary chemical means have been called "Isotopes" by Soddy.

The rule advanced by Soddy,²⁰ Fajans,²¹ and others, that the expulsion of an alpha particle causes the element to shift its position in the periodic table two places to the left, and to decrease in atomic weight by four units is also in accord with the theory if we consider that the alpha particle comes from the nucleus of the atom. Similarly the expulsion of a beta particle, which is a negative electron, would cause the element to shift its position in the table one place to the right, without any change of mass. In this case the positive charge on the nucleus is increased by one unit.

In radioactive changes the expulsion of a beta particle, which evidently is shot out of the nucleus, as is shown by its extremely high velocity, causes the element to move one group to the right in the periodic table, which means an increase of one in the atomic number. From this it seems evident that this gives a proof, at least for the radioactive elements, and probably in the case of all lower atomic weight elements, that an increase of one in the atomic number means an increase of one in the positive charge on the nucleus. It seems probable, therefore, that the number of positive charges on the nucleus is equal to the atomic number.

TABLE I.

| Element. | Radiation. | Valence. | Atomic no. | Atomic wt. |
|--------------------------------------|----------------|----------|------------|------------|
| Ur I..... | α | 6 | 92 | 238 |
| UrX ₁ | β | 4 | 90 | 234 |
| UrX ₂ | β | 5 | 91 | 234 |
| Ur II..... | α | 6 | 92 | 234 |
| Io..... | α | 4 | 90 | 230 |
| Ra..... | α | 2 | 88 | 226 |
| Ra Em..... | α | 0 | 86 | 222 |
| Ra A..... | α | 6 | 84 | 218 |
| Ra B..... | β | 4 | 82 | 214 |
| Ra C..... | $\beta \alpha$ | 5 | 83 | 214 |
| Ra C ₁ | $\alpha \beta$ | 6 | 84 | 214 |
| Ra C ₂ ¹ | $\alpha \beta$ | 3 | 81 | 210 |
| Ra D..... | β | 4 | 82 | 210 |
| Ra E..... | β | 5 | 83 | 210 |
| Ra F..... | α | 6 | 84 | 210 |
| Pb..... | ... | 4 | 82 | (206) 207 |

| Element. ² | At. wt. | At. no. | Element. | At. wt. | At. no. |
|-----------------------|---------|---------|-------------------------|---------|---------|
| Ur I..... | 238 | 92 | Ur X ₁ | 234 | 90 |
| Ur II..... | 234 | | Io..... | 230 | |
| Ra A..... | 218 | 84 | Ra B..... | 214 | 82 |
| Ra F..... | 210 | | Ra D..... | 210 | |
| | | | Pb..... | 206 | |

¹ According to recent work by Miss Meitner there seems to be considerable doubt as to the existence of RaC₂.

² This table gives only the isotopes of the radium series.

The work of Rutherford and Andrade²² serves to further confirm these views. The wave length of the soft γ rays from Ra B was determined, and also the X-ray spectrum of lead, with a view to determine the atomic numbers of these and the other radioactive elements. Ra B and lead were found to have the same atomic number, 82, as they gave the same X-ray spectrum. From Table I it is seen that there are several groups of elements having the same atomic number but with different atomic weights. These are tabulated at the bottom of Table I.

It will be noted that the atomic weight of lead, if its source is the uranium series of elements, should be 206.18, using the latest value of the atomic weight of uranium as 238.18. The atomic weight of lead has recently been determined by Richards,²³ who obtained the value 207.15 for ordinary lead, not radioactive. In analyzing the lead from a large number of radioactive minerals, mostly uranium, he obtained values varying from 206.4 to the ordinary value, 207.15. Soddy,²⁴ working with thorium minerals, obtained the value 208, which would be expected if the end of the thorium series is also lead. More recently Soddy²⁵ has started a more extensive investigation, and has obtained about 80 grams of lead from thorium minerals. He finds that the lead has a higher density than the ordinary lead. This is to be expected if the atomic volumes of the isotopes are the same. Richards found no difference between the spectrum of the lead of low atomic weight and the ordinary lead, but Soddy claimed to have found at least one line in the new material which was not given by the old. In some work as yet unpublished, done by Aronberg working with Gale and one of the writers, no difference was found between the spectrum of some lead from Carnotite and the ordinary lead, although the Zeeman effect was also investigated. In this investigation a 21 foot concave grating was used, and the wave lengths could be measured to 0.001 of an Ångström.

Lindemann* shows by means of simple thermodynamical reasoning that two elements of different atomic weight must differ either in their chemical or physical properties. Since Soddy has shown that the isotopic forms of lead have the same atomic volumes, and also, of course, the same chemical properties, it follows that the forces between the atoms, and therefore the vapor pressures and the melting points, must vary, and that Soddy's lead from thorite should have a melting point 1.54 degrees higher than ordinary lead. Lindemann concludes that the forces of attraction and repulsion between the atoms have their origin in the nucleus, while, as is generally considered, the chemical properties and the radius of the atom are conditioned by the external electrons. In isotopes the forces of attraction and repulsion are proportional to the atomic weight, that is, probably to the number of positive particles. These forces are, however,

* *Nature*, March 4, 1915.

not usually additive, but are so only in isotopes, so the nuclei of isotopes probably differ in their linear dimensions, but not at all, or very little, in the arrangement of the particles. The question as to the melting point of lead from carnotite is now being investigated by one of the writers of this paper.

The fact that α particles are expelled in so many of the transformations seems to show that the nucleus is composed, in part at least, of helium atoms. The energy of the expulsion of the alpha particles can be accounted for by their passage through the intense electric field around the nucleus. The primary beta particles probably arise from a disturbance of the nucleus, which must be very complex.

The general facts which seem to be proved by all this work described above are, that the nucleus is a fundamental constant of matter, and that the charge on the nucleus determines the character of the element. The atomic weight is not so characteristic as the atomic number or the nuclear charge. The atomic weight is a complex function of the number and configuration of the electrons. Those properties of matter such as gravitation and radioactivity, which are entirely beyond our control by any chemical or physical agents, are functions of the nucleus.

Up to this point, beyond the fact that the atom is a sort of Saturnian system, nothing has been said as to the arrangement of the electrons in the atom, or the distribution of the forces. The first attempt to treat this problem as one of mechanics, and to give a definite picture of the atom, was made by Bohr.²⁶ In his calculations, Bohr has used an atom of the Rutherford type, and has combined with the classical mechanics Planck's quantum hypothesis. While Bohr's work has been severely criticized, the very remarkable results he was able to obtain with hydrogen alone make it worthy of careful consideration. Bohr's success lies only in the consideration of atoms with one vibrating electron. The following is a simplified form of his analysis:

Let m = mass of the electron.

$-e$ = charge of the electron.

M = mass of nucleus.

E = charge on nucleus.

a = radius of ring of rotation of electrons.

ω = frequency of revolution of electrons.

Then, $2\pi\omega$ = angular velocity.

The kinetic energy of an electron can be expressed in two ways:

$$\frac{1}{2} m(2\pi\omega a)^2 \quad \text{or} \quad \frac{1}{2} eE/a.$$

The work necessary to remove an electron from its orbit to a position of rest at ∞ is:

$$eE/a - \frac{1}{2} m(2\pi\omega a)^2 = \frac{1}{2} (eE/a) = W.$$

Then

$$2a = eE/W \quad \text{and} \quad \omega = \frac{\sqrt{2}}{\pi} \frac{W^{3/2}}{eE \sqrt{m}}.$$

According to Newtonian mechanics, the energy W should go on increasing as energy is given out by radiation, until the orbit gets smaller and smaller and the electron falls into the nucleus; that is, " a " would decrease and ω increase. Here Bohr introduces the quantum hypothesis. He assumes that the angular momentum of the electron is constant, and equal to $\tau h/2\pi$, where τ is an integer, and h is Planck's constant; that is, the angular momentum of the electron in its orbit is

$$2\pi m \omega a^2 = W/\pi \omega = \tau h/2\pi.$$

This prevents continuous variations of W , a , and ω .

Then,

$$W = \frac{2\pi^2 m e^2 E^2}{\tau^2 h^2} \quad 2a = \frac{\tau^2 h^2}{2\pi^2 m e E}.$$

Much of the criticism of Bohr's work is directed at this point in his analysis. The idea of an electron undergoing accelerated motion without radiating energy is difficult to accept. There is also difficulty in obtaining any satisfactory physical picture of the process by which light is emitted when the electron changes from one steady state of vibration to the next, as described below.

In a neutral hydrogen atom τ is equal to 1. If this value is substituted in the second equation, the value for the diameter of the hydrogen atom is obtained as 1.1×10^{-8} cm., which is of the right order of magnitude.

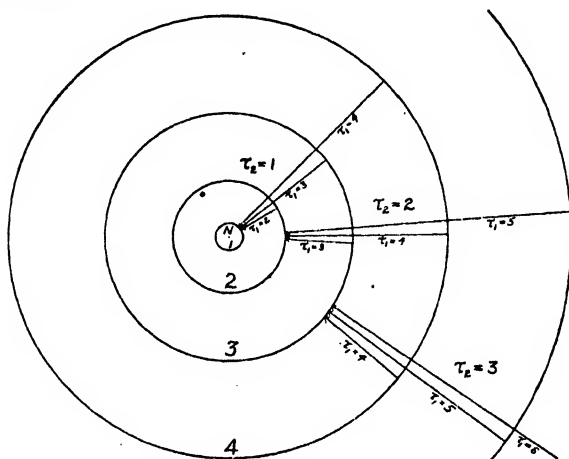
The electron radiates energy only when it changes from one steady state of vibration to another, and then one quantum of energy is released; that is, for a sudden shrinkage from orbit of τ_2 to τ_1 , there must be a loss of energy $W = h\nu$ where ν is the frequency of the radiation.

$$h\nu = \delta W = W_{\tau_2} - W_{\tau_1} = \frac{2\pi^2 m e^2 E^2}{h^2} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right) \\ = \frac{2\pi^2 m e^2 E^2}{h^3} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right).$$

In the case of hydrogen, $E = e$. We can then calculate the value of the constant $2\pi^2 m e^2 E^2/h^3$ which is equal to 3.26×10^{15} . The well-known Balmer formula for the series of lines in the hydrogen spectrum is $\nu = K (1/\tau_2^2 - 1/\tau_1^2)$ in which K as determined by experiment is 3.29 times 10^{15} . This practical identity of Bohr's calculated value of the Rydberg constant and the experimental value is probably the greatest triumph of Bohr's work.

If the value 1 is assigned to τ_2 , and a series of values, 1, 2, 3, etc.,

given to τ_1 , the frequencies of a series of lines in the ultraviolet are determined. This series was not known at the time of Bohr's first work, but has since been found by Lyman of Harvard. (Not published.) The physical picture obtained of the production of this series of spectrum lines is as follows:



N represents the nucleus of the atom. The rings 1, 2, and 3 correspond to the orbits of the electron in the various steady states of motion. When an electron falls from one steady state to the next one of smaller radius of vibration, one quantum of energy is liberated. In the above spectral series, all the lines are formed by electrons falling from the second ring and beyond, all the way to the first ring. The first line in the series is due to an electron falling from the second to the first ring; the second line to an electron falling from the third to the first ring, and so on.

If $\tau_2 = 2$, and a series of values be assigned to τ_1 , the ordinary Balmer series for hydrogen results. For $\tau_2 = 3$, there results an infra-red series predicted by Ritz, and later discovered by Paschen. This model does not account for the Pickering series of lines which is ordinarily attributed to hydrogen, but Bohr shows that this series is accounted for by the helium atom.

Very recently another confirmation of Bohr's theory has been given by Evans²⁷ in his work on the spectra of hydrogen and helium. Bohr's formula, when modified so as to take account of the mass of the nucleus, is

$$\nu = \frac{2\pi^2 e^2 E^2 M m}{h^3 (m + M)} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right).$$

This makes a slight change in the value of the constant in passing from hydrogen to helium, and the ordinary Balmer series for hydrogen, which according to Bohr's original work could come from either of the two

elements, is found to be slightly different for the one than for the other. Thus it became very important to investigate carefully the spectra of these two elements, and see if this series could be detected in helium, and whether the slight differences just spoken of existed. Evans was able to observe the first few members of this series, and the measured values of the lines are very close to the theoretical.

Bohr²⁸ has also shown that if the principle of relativity is introduced, his formula takes the following form, which accounts for some of the extremely small errors found by Evans.

$$= \frac{2\pi^2 e^2 E^2 m M}{h^3 (m + M)} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right) \left[1 + \frac{\pi^2 e^2 E^2}{c^2 h^2} \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right) \right].$$

Helium is considered to have a charge on its nucleus of $2e$, or $E = 2e$. The atom with one positive charge has one vibrating electron. The following formula results for helium:

$$= K \left(\frac{1}{(\tau_2/2)^2} - \frac{1}{(\tau_1/2)^2} \right)$$

The physical interpretation is the same as for hydrogen. For various values of τ_2 , the following series result:

$\tau_2 = 1$ —Extreme ultraviolet; not known.

$\tau_2 = 2$ —Extreme ultraviolet; not known.

$\tau_2 = 3$ —Two series, as τ_1 is odd or even. (The lines of the two series alternate.) These series were observed by Fowler in mixtures of hydrogen and helium, but had been attributed to hydrogen.

$\tau_2 = 4$ —The lines of two series, alternating as τ_1 is odd or even. The first of these is the ordinary Balmer series, which evidently can come from either hydrogen or helium. The second is a series which was observed by Pickering in the star ζ -Puppis, and was attributed to hydrogen.

In the work of Evans which was mentioned, there is a further confirmation of Bohr's theory. By carefully adjusting conditions he was able to obtain the Pickering series of lines from absolutely pure helium, which should be the source of them, according to Bohr.

Balmer's series has never been observed in the laboratory beyond $\tau_2 = 12$, while in stellar spectra it extends to $\tau_2 = 33$. Therefore in vacuum tubes no hydrogen atoms exist of greater diameter than corresponds to $\tau_2 = 12$, or $2a = 1.6 \times 10^{-8}$ cm. For $\tau_2 = 33$, $2a = 1.2 \times 10^{-5}$ cm. Therefore, according to Bohr's theory, there are in the stars hydrogen atoms 1000 times the diameter of those on the earth.

Jeans³¹ points out that in the above work the value of M is supposed to be very great in comparison with m . If this is not true, the value of Rydberg's constant is given by

$$K = \frac{2\pi^2 e^2 E^2}{h^3} \frac{mM}{(m + M)}.$$

If M refers to the value for hydrogen, $2M$ is the value for helium. Then $K_H : K_{He} = \frac{4}{M + 1/2m} : \frac{1}{m + M}$. From the best observed value of the ratio K_H/K_{He} , M/m is given as 1836 ± 12 , which is in close agreement with the experimental value.

The above calculation would seem to be inconsistent with the idea of the atom as developed by Rutherford, for he states that practically all of the mass of the atom lies in the nucleus. In that case, the value of M for helium would not be *twice* but *four* times the value for hydrogen, and the helium nucleus would consist of four positive and two negative electrons.

Bohr extends his calculations to the lithium atom, and in considering only one vibrating electron obtains good results. In all of his work, however, when more than one electron is considered, his results are not correct. One of the serious objections to Bohr's theory is that he has been unable to explain the ordinary spectrum of hydrogen. Nicholson²² has extended Bohr's calculations to every possible mode of vibration in attempting to secure a formula or formulas, giving the lines of the ordinary hydrogen spectrum, but has found that they can be accounted for by no possible vibration.

Perhaps the most fundamental objection to Bohr's work lies in the fact that he has combined two basically different kinds of mathematics in working out this theory. It might be possible under such conditions to obtain results which are absolutely incorrect, for the two are contradictory.

Nicholson claims to have proven both by the classical mechanics and by Bohr's mechanics that coplanar, concentric rings of vibrating electrons are unstable. That is, if there are to be two or more rings of electrons in an atom, they cannot lie in the same plane, which would make Bohr's theory untenable. This presents difficulties in still another way. If we consider valence as due to certain electrons which are ordinarily considered as being near the outside of the atom, these electrons would either have to be in an outer ring, by themselves, or else have some peculiar properties different from the other electrons in the ring. J. J. Thomsen not only believes in the existence of more than one ring of electrons, but in some work yet unpublished, states that he has actually counted the number of rings in certain atoms. This claim of Nicholson's would seem to be wrong, but it may be very true, as he says, that a large number of the vibrations in such a system are unsteady, and would result in the expulsion of an electron.

Bohr has not had better success in accounting for a large part of the

spectrum of helium than he had in the case of hydrogen. Helium has six Balmer series which are not explained. Bohr considered only the first electron in his calculations on this element, and Nicholson thought that possibly the rest of the spectrum might be due to the other electron. He therefore made the necessary calculations, but could obtain no other series. Two of the series of lines calculated for helium lie in the ultra-violet, and are not known. Lyman of Harvard, as a result of his investigations, states that helium has no Schumann region spectrum.

It is well to remember that Bohr attempts no physical picture or cause of the change of an electron from one steady state of vibration to the next. In his theory of spectra, the energy which goes into the spectrum is atomic energy. This would be a serious objection if it were not for the fact that it is very easy to think of it in a slightly different way. The energy which it is necessary to apply to hydrogen to give these spectral lines may be used to remove an electron from one of the inner rings of vibration to one farther out from the nucleus. This is equivalent to increasing the atomic energy, and the increase, which came from an outside source, is given out as monochromatic radiation when the electron falls toward the nucleus.

Of the work on the structure of the atom none is more interesting than that of Nicholson, a number of his predictions from a theoretical standpoint having been confirmed in a most spectacular way. His work is also of extreme interest to chemists, since it deals with elements which have not as yet been discovered on the earth. For a considerable time it has been known that there are at least two important elements which are recognized by their spectrum, but which have not as yet been discovered on earth. A number of spectral lines of unknown origin were known to be given by the corona of the sun, and these were attributed to an element coronium, while the lines of unknown origin emitted by the nebulae were supposed to be due to an element which was given the name *nebulium*. The chief line of its spectrum is the line $\lambda 5007$. Nicholson was able, by the assumption that certain lines belong to the spectrum of *nebulium*, to calculate the wave lengths of all of the other lines but two, for which he was altogether unable to account. Just at the time when Nicholson made his calculation, Wolf of Heidelberg was engaged in the study of these same lines in the spectra of the nebulae, and he found that certain lines, which had formerly been attributed to *nebulium*, acted differently from the others. He found, for example, that in the ring nebula in Lyra, discovered by Darquier in 1779, certain of these lines were emitted by the interior, and others by its outer part. The remarkable part of this discovery was that the two lines which were thus shown to have different origin from the true lines of *nebulium*, were just the two lines which Nicholson was unable to connect theoretically with the spectrum

of nebulium. Another of Nicholson's predictions, which was confirmed in a remarkable manner, was that of the existence of a new nebulium line of wave length 4352.9. On photographing the spectrum, Wright, of the Lick observatory, found this line, and on looking over his older photographs, he found the line on a plate taken several years before the prediction of its existence was made, but the line was so weak that it had escaped observation.

In an extremely long series of papers Nicholson³⁰ has arrived at a very comprehensive theory of spectra, and has applied it to such problems as cosmic evolution. It gives a picture of operations in vast nebulae, many light years in extent, in connection with atomic and subatomic structure; changes occupying milleniums of time are discussed in connection with those occurring in a fraction of a second. Its very comprehensiveness causes some skepticism, but the remarkable results he has obtained would seem, in part at least, to justify the theory.

Nicholson also uses an atom of the Rutherford type, in which the electrons are vibrating in orbits around the positive nucleus. All of Nicholson's work is, however, based on calculations made by the classical mechanics. The quantum hypothesis is not introduced to obtain any of the results, but in the course of his work, Nicholson shows how the results seem to be related to this hypothesis.

One of the interesting points of this theory is that the energy which goes into the spectrum is secured from the outside, and is not, as originally in the theory of Bohr, atomic energy. This would seem to be much more probable.

The electrons are considered as moving in a steady state, in a ring around the nucleus. Outside forces acting on these cause them to take up a vibration perpendicular to the plane of the ring. There are several modes of vibration, depending on the number of electrons in the ring. The strongest vibration would have a frequency equal to the frequency of the electrons in the ring. This is expressed by $q = \omega$, or $q/\omega = 1$. In vibrations of class zero the entire ring vibrates as a whole, always keeping parallel to its original position. The second class of vibration consists in the ring vibrating in halves. That is, there are two nodes and two crests in the wave which travels around the ring. It is evident that there are as many classes of vibrations as there are electrons in the atom. The vibrations of the higher classes would not be expected to be strong, and Schott has shown that the vibrations of a class higher than three would not ordinarily be strong enough to see. The mathematical analysis is largely the same as that developed by J. J. Thomson in his work on his atomic model, and will not be given completely here. Only the results which are used directly will be reproduced.

e = charge on an electron.

a = radius of the ring.

ν = no. charges in nucleus.

m = mass of an electron.

q/ω = frequency of revolution.

The equation for the period of vibration which Nicholson obtains is

$$mq^2 = e^2/8a^3 (8\nu + P_k + P_o)$$

where

$$P_k = \Sigma^{n-1} (\cos 2K \pi/n \csc^3 \pi/n)$$

and

$$P_o = \Sigma^{n-1} (1 \cdot \csc^3 \pi/n).$$

There may be as many values of the period as there are of P_k , which is as many as the number of electrons. k is called the class of the vibration.

The first atom which Nicholson considered was one in which the number of positive charges in the nucleus is four. That is, $\nu = 4$. This atom he has called nebulium. First consider the neutral atom, in which there are four negative electrons. The period equation may be written as

$$ma^3q^2 = e^2 [\nu + (P_k - P_o)/8], \quad k = 0, 1, 2, \text{ etc.}$$

If ω = the angular velocity of the ring, the force of an electron towards the center is $ma\omega^2$. The radial attraction of the positive nucleus is $\nu e^2/a^2$. The combined action of the other electrons gives a radial repulsion of $e^2 S_n/4a^2$ where $S_n = \Sigma^{n-1} \csc \pi/n$. Therefore,

$$ma\omega^2 = e^2/a^2 (\nu - S_n/4) \quad \text{or} \quad e^2/ma^3 = \omega^2 (\nu - S_n/4)$$

is the equation for the steady state of the neutral atom. The period equations of this system then become

$$q^2/\omega^2 = \frac{16}{15-2\sqrt{2}}, \quad k = 0$$

$$= 1, \quad k = 1 = 3$$

$$q^2/\omega^2 = \frac{8}{8+\sqrt{2}}, \quad k = 2$$

or

$$q/\omega = (1.146533, 1, 0.849778)$$

Correcting for a stationary observer, and introducing negative values of k ,

$$q/\omega = (1.146533, 1.150222, 2, 2.849778, 4)$$

$$k = 0 \quad k = -2 \quad k = 1 \quad k = 2, \quad k = 3$$

In wave lengths (C = velocity of light) and considering a vibration in the plane where $q = \omega$, which we would expect to be strong,

$$\lambda = 2\pi C/\omega (1, 0.872194, 0.86939).$$

The first value is for $q = \omega$, the second for $k = 0$, the third for $k = -2$.

The chief nebular line is $\lambda = 5006.9$. If this is chosen as the fundamental line, then $(5006.9)(0.872194) = 4367.0$ should be the next line of this set. A strong line is known at 4363.4. Also $(5006.9)(0.86939) = 4352.9$ should be the next. At the time of this work, no line was known at 4352.9 but it was afterward found by Wright³¹ of the Lick Observatory, and measured as 4352.3. Nicholson made similar calculations for this atom with 2, 3, 5, and 6 electrons. The results are given below:

| | $q = \omega.$ | $k = 0.$ | $k = 1.$ | $k = 2.$ | $k = -2.$ | $k = 3.$ |
|---------|----------------------------------|-----------------|-----------------|----------|----------------|----------|
| $n = 6$ | $\lambda = 2\pi C/\omega \times$ | | 1 | 0.81934 | | (0.6666) |
| | $\lambda =$ | | 4959. <i>a</i> | 4063.2 | | |
| | Observed..... | | 4959 | 4059.0 | | |
| $n = 5$ | $\lambda = 2\pi C/\omega \times$ | 1 | 0.80991 | | 0.81573 | |
| | $\lambda =$ | 4743.0 | 3838.9 <i>a</i> | | 3869. <i>a</i> | |
| | Observed..... | 4740.0 | 3835.8 | | 3869. | |
| $n = 3$ | $\lambda = 2\pi C/\omega \times$ | 1 | 0.9250 | | | |
| | $\lambda =$ | 4026.8 <i>a</i> | 3724.8 | | | |
| | Observed..... | 4026.8 | 3729.0 | | | |
| $n = 2$ | $\lambda = 2\pi C/\pi \times$ | 1 | 0.96826 | | | |
| | $\lambda =$ | 3967.6 <i>a</i> | 3841.5 | | | |
| | Observed..... | 3967.6 | 3835.8 | | | |

"*a*" placed after a wave length shows that this one was assumed for that particular series.

The first method of attack used by Nicholson is briefly this, as is seen from the previous work. Making use of the theoretical analysis, he obtains the ratios of the wave lengths of what might be called a series, but not their absolute values. If a value for one of them is assumed, the rest are given. The agreement in some cases is far from good, and later it was found necessary to consider certain of the lines as due to a different source than given here. It is not clear as to why in the series for $n = 5$ for instance, the line for $k = -2$ should appear, and not the one for $k = 2$, or for the vibrations which should be still stronger, $k = 1$.

It will be seen that there is an error of about 4 \AA° in a large number of these calculated wave lengths. Nicholson shows that, except in the case of the vibration of Class O, this can be accounted for by the fact that the velocity of the electron is not small compared with that of light, or at least is not small enough so that it can be neglected without error. He calculates that the error due to this cannot be greater than about one part in a thousand, which amounts to about 4 \AA° with the wave lengths considered.

Bromwich pointed out to Nicholson that in the case of the vibration of Class O, the mass of the electron and the nucleus did not cancel out, but that a correction term of the form

$$(1 + nm/M)$$

should be introduced into the period equation. If H is the value of M for a hydrogen atom, then

$$m/H = 0.00054 \text{ approximately.}$$

This makes it possible to calculate the atomic weight of nebulium, which gives the value 1.3.

Using this method of ratios, Nicholson has calculated the wave lengths of lines for systems of $\nu = 2, 3, 5$, and 6. For $\nu = 2$ and 3, the lines were found by Wolfe in the nebulae. $\nu = 5$ was found in the solar corona, where Nicholson accounted for 21 out of 27 lines found.

For the systems $2e$, $4e$, $5e$, and $6e$, calculations have been made for the atomic weight by the method described above. From the values obtained, it can be shown that the atomic weights of these simple ring systems are proportional to the squares of the number of charges on their nuclei. For the entire series, the results are as follows:

| | | | | | | |
|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Element..... | Pr.H | ... | ... | Nu | Pf | Arc |
| Atomic no..... | 1e | 2e | 3e | 4e | 5e | 6e |
| Atomic wt..... | 0.082 | 0.327 | 0.736 | 1.31 | 2.1 | 2.9 |
| Ratio..... | 1 ² | 2 ² | 3 ² | 4 ² | 5 ² | 6 ² |

Here is a relation involving N^2 as in Moseley's work.

Up to this point, Nicholson used his method of ratios, and thus calculated the wave lengths of the most of the unknown lines in the nebulae and the solar corona, and succeeded in securing approximate values for the atomic weights. No connection has as yet been shown to exist between the systems of different nuclear charge. This relation is brought out later. Also, no relation has been shown between the principal frequency of vibration of the systems of the same nuclear charge, with varying numbers of electrons. This relation is shown by the consideration of the energy of the systems involved.

As Nicholson points out, it is impossible to know the absolute energy of the atom,¹ but changes of energy may be used. By a very simple analysis Nicholson arrives at the following equation of energy of the atom, in which the term D is equal to the energy in a standard configuration:

$$\frac{1}{2} mnv^2 = ne^2/a (\nu - \frac{1}{4} S_n) + D$$

By the condition of steady motion,

$$ma^3\omega^2 = e^2 (\nu - \frac{1}{4} S_n) = m\omega v^2.$$

Now, $\omega = 2\pi C/\lambda'$, where λ' is the principal wave length. This gives

$$mna^2\omega^2 \cdot \frac{2\pi}{\omega} = \frac{mn}{C} \left\{ \frac{e^2}{m} (\nu - \frac{1}{4} S_n) 2\pi C \right\}^{1/2} \lambda'^{1/2}.$$

¹ Equations have been developed from the standpoint of both the electromagnetic theory and the theory of relativity, which give the total energy of an atom in terms of its mass, but it is of course, not certain that these equations are valid.

Therefore it is seen that the ratio of energy to frequency is proportional to $n(\nu - 1/4 S_n)^{1/2} \lambda^{1/2}$, and for convenience this will be called the atomic energy, E . Then $E = n(\nu - 1/4 S_n)^{1/2} \lambda^{1/2}$.

Now the calculation of E for the various atoms of protofluorine where $\nu = 5$, gives the following result:

| | $n = 5.$ | $n = 4.$ | $n = 3.$ | $n = 2.$ |
|-----------|----------|----------|----------|----------|
| E | 187.04 | 164.6 | 134.7 | 97.4 |

If 7.482 is chosen as the unit of energy, the number of units for the different systems is as follows:

| | $n = 5.$ | $n = 4.$ | $n = 3.$ | $n = 2.$ | $n = 1.$ | $n = 0.$ |
|-------------------------|----------|----------|----------|----------|----------|----------|
| | 25 | 22 | 18 | 13 | 7 | 0 |
| Differences..... | | 3 | 4 | 5 | 6 | 7 |
| Units per electron..... | 5 | 5.5 | 6 | 6.5 | 7 | |

It is now possible to calculate the wave length of the line of principal frequency for the system $n = 2$. For this system it is seen that there are 6.5 units of E per electron, therefore

$$E = 2 (6.5 \times 7.482) = 2 (5 - 1/4 S_2) \lambda^{1/2} \quad (S_2 = 1.000).$$

From this $\lambda = 5073$. A weak line is known at this point.

If the energy of one of these systems is decreased by radiation by certain discrete amounts, we would expect a series of lines of some sort to be the result. That is, a series of spectrum lines might emanate from atoms whose internal angular momenta have run down by discrete amounts from a standard. In the case of protofluorine with two electrons, the loss of energy would be expected to be large enough so that the series could be observed. The wave lengths of the lines of this series may be expressed by the formula

$$\lambda = (97.107/2 - 1.223r)^3 / (4.75)^2.$$

That is, the energy E is being decreased by an amount 2.2446 each time. The term r takes successively the values 1, 2, 3, etc. The series is as follows:

| r | 0 | 1 | 2 | 3 | 4 | 5 | 6 |
|-----------------|------|------|------|--------|------|------|------|
| Calculated..... | 5073 | 4725 | 4400 | 4086.5 | 3788 | 3506 | 3238 |
| Observed..... | 5073 | 4725 | 4400 | 4087.4 | .. | 3505 | .. |

All these are weak lines. It may be pointed out that this method of calculating a series is very similar to Bohr's method where he decreases the internal energy of the atom by discrete amounts to give the members of the series. Bohr has given some sort of an idea as to how this takes place, while Nicholson merely states that the energy is lost by radiation. Such vibrations as give rise to this type of series are vibrations in the plane of the ring, as in Bohr's model. It will be noted later that Nicholson makes considerable use of this method, even discarding his original identifications of some of the nebular and protofluorine lines, and putting them into series of this type.

If Q equals the number of quanta of energy per electron, choosing as a unit the value $h/5$, where h is Planck's unit, a still more useful equation is obtained,

$$Q = E/n = \frac{\lambda^{1/2} (\nu - 1/4 S_n)^{1/2}}{0.06235}.$$

For the atom of protofluorine where $\nu = 5$, the various values of Q are as follows:

| | | | | |
|-----------|-----|-------|-----|-------|
| n | 5 | 4 | 3 | 2 |
| Q | 600 | 658.5 | 718 | 778.5 |

These values of Q can easily be shown to be in the ratio of 10 : 11 : 12 : 13 : 14.

In the case of Pf just dealt with, the value of Q may be expressed by a function of the following type:

$$Q = A + Bn + Cn^2$$

where A , B , and C are constants. If such a formula is to be applied to other atoms than Pf, these terms may not be constants, but functions of the nucleus. Since the function E/n has been shown to be harmonic, it may be supposed that the function E/ν would be of the same general type, that is:

$$E/\nu = \alpha + \beta\nu + \gamma\nu^2,$$

where $\nu = n$, a neutral atom. Therefore the function E/n for any atom is of the form

$$E/n = A + B\nu + C\nu^2 - n(D + E\nu) + Gn_2.$$

Since E in all cases is very closely a multiple of Planck's unit, the constants A to G will be close to whole numbers. The divergencies might be due to the rotation of the nucleus of the atom as a whole, at the expense of the angular momentum of the system, which otherwise might be exactly a multiple of $h/2\pi$. Nicholson calculates the values of these constants from the case of Pf, and then uses this method for the recalculation of the lines of the system $4e$, nebulium. He finds that it is necessary to change the source of a number of the lines from that given them by his first method. More of them are now thought of as coming from vibrations which fall into the type of series where the cube roots of the wave lengths differ by constant amounts, as in the series calculated for the system $\nu = 5$, $n = 2$. The value of Q for such series can be found from a formula of the type used in the series just referred to:

$$Q = (Q_n/18r),$$

where r is variable, taking successively the values 1, 2, 3, etc.

The law relating the number of quanta of positive and negative systems is:

$$(E/n)_{r-m} + (E/n)_{r+m} = 2(E/n)$$

A series might arise from negatively charged systems, from the energy disturbances due to the repulsion of negative electrons by the system. Such series might be expected to be quite strong. A neutral system would be unaffected by electrons, only becoming ionized by virtue of its own unstable vibrations.

Some very important relationships may be brought out by the consideration of the relations between the energy of the various neutral systems of different nuclear charge. If the principal wave length of the system is known, it is possible to calculate the value of E/n from the formula

$$E/n = \frac{\lambda^{1/2} (\nu - 1/4 S_n)^{3/2}}{(0.06235)}.$$

The values of E/n for the systems $\nu = 5, 4$, and 2 are 600, 576.08, and 374.04, respectively. These are three terms of the following harmonic sequence:

| | | | | | |
|---------------------|-------|--------|--------|--------|--------|
| ν | 5 | 4 | 3 | 2 | 1 |
| E/n | 600 | 576.08 | 500.76 | 374.04 | 195.92 |
| Difference..... | 23.92 | 75.32 | 126.72 | 178.12 | |
| Second difference.. | | 54.40 | 54.40 | 54.40 | |

As stated before, it might be expected that these values of E/ν , which are obviously the same as E/n , could be expressed by the formula

$$E/\nu = \alpha + \beta\nu + \gamma\nu^2.$$

The following three equations can be solved for the constants:

$$600.00 = \alpha + 5\beta + 25\gamma \quad (1)$$

$$576.08 = \alpha + 4\beta + 16\gamma \quad (2)$$

$$500.76 = \alpha + 3\beta + 9\gamma \quad (3)$$

and $\alpha = -32$, $\beta = 254.4$, $\gamma = -25.6$. Therefore

$$Q = E/\nu = 254.4\nu - 25.6\nu^2 - 32.$$

If the values of E/ν for the systems 6e, 7e, 8e, 9e and 10e are calculated the following results are obtained:

| | | | | | |
|---------------|--------|--------|--------|--------|--------|
| ν | 6 | 7 | 8 | 9 | 10 |
| E/ν | 572.52 | 493.64 | 363.36 | 181.68 | -51.40 |

The fact that for $\nu = 10$ the energy is negative points to the fact that there are only 9 simple ring systems possible. If the first one is left out of consideration, and hydrogen is not put in the periodic table, the number of simple ring systems is the same as the number of groups in the first two rows of the periodic table. It will be shown later that the simple ring system 1e is very closely related to hydrogen so that leaving them both out of consideration at this point has some justification, particularly as the place of hydrogen in the table is very uncertain.

Knowing the value of E/ν for the various systems, it is possible to find their principal frequencies from the following formula:

$$\lambda = \left(\frac{E \cdot 0.06235}{\nu} \right)^3 \frac{1}{(\nu - 1/4 S_n)^2}$$

| | | | | |
|-----------------|---------|---------|--------|-------|
| ν | 6 | 7 | 8 | 9 |
| λ | 2613.57 | 1323.12 | 431.02 | 45.15 |

All these are outside of the range of observation, but it will be shown later that the first of these exists in the nebulae, and it has been given the name arconium. It will also be shown that the system $1e$ exists, and it has been given the name protohydrogen. Its principal wave length is calculated as 1823.55, which is exactly one-half the limit of the Balmer formula for hydrogen.

The system $2e$ is present in the nebulae, and in *Nova Persei*. The atom with nucleus $3e$ is also present in the nebulae, but its lines are not as strong as those of $2e$. The system $4e$ is nebulium and gives rise to the strongest nebular lines. Protofluorine, $5e$, has not been found in the nebulae, but is one of the main constituents of the solar corona. As just stated, $6e$, arconium, and the system $7e$ are found in the nebulae.

The remarkable agreement of these theories of Nicholson's with the facts would seem to indicate that there is here an extremely broad foundation for a system on which the building up of the chemical elements may rest. The relations between the energy of these systems seems to indicate that the principle of the constancy of angular momentum may be the physical basis of Planck's theory and also the basis of all the possible arrangements of electrical charges into the form of ordinary matter.

One of the most important and interesting pieces of work which Nicholson has done is in connection with the spectra of the Wolf-Rayet stars. These stars are considered by the astronomers as the earliest type known. They are regarded as being some sort of evolution product of the nebulae. The only ordinary elements which are present are hydrogen and possibly helium, although the last is not well represented unless, as Bohr suggests,* the Pickering series is due to this element. Nicholson shows that a number of Balmer series exist in these stars, and identifies them in a remarkable manner with the constants of the simple ring system called nebulium.

If the lines of these stars are examined they are found to contain a number of lines in the ratio of 5/4. Thus:

$$\begin{array}{ll} 5285/4228 = 1.2500 & 5693/4555 = 1.2499 \\ 5813/4652 = 1.2495 & 5593/4473 = 1.2503 \end{array}$$

If the Balmer formula is considered for one special case the following relationship is found:

$$\lambda = \lambda_0 m^2 / m^2 - 1$$

For $m = 2$ and 4 the following results:

$$\lambda_2 = 4/3 \lambda_0 \quad \lambda_4 = 16/15 \lambda_0 \quad \lambda_2/\lambda_4 = 5/4$$

* This suggestion is confirmed by the work of Evans.

This suggests that Balmer series exist in the Wolf-Rayet stars, and a simple calculation gives the following:

$$\lambda = (4104, 3963.5) m^2/m^2 - 1$$

A further examination of the lines leads to the following four series:

$$\lambda = (4104, \text{ or } 3963.5) \left(\frac{m^2}{m^2 - 1} \text{ or } \frac{m^2}{m^2 - 0.3286} \right)$$

It was found in the previous work that the three main vibrations of the neutral nebulium atom had frequencies in the following ratio:

$$q^2/\omega^2 = 1, 1.3145, 0.8496$$

Now $0.3286 = 1.3145/4$. This shows that these series are in some way related to the nebulium atom. It seems probable that another series or rather two series might exist in which the term 0.3286 was replaced by one-fourth of the other ratio for the third line of the neutral atom.

$$0.8496/4 = 0.2124.$$

The formula would then be

$$\lambda = (4104, 3963.5) m^2/m^2 - 0.2124.$$

Lines calculated for $m = 2$, and 3 give lines which are known in these stars, thus confirming the theory.

In general then, the formula for the Balmer series in the Wolf-Rayet stars may be written as

$$\lambda = (4104, 3963.5) \left(\frac{m^2}{m^2 - q^2/4\omega^2} \right).$$

A search for another limiting frequency gives the value 5254. We now have nine Balmer series which may be written as

$$\lambda = (4254, 4104, 3953.5) \left(\frac{m^2}{m^2 - q^2/4\omega^2} \text{ or } \frac{m^2}{m^2 - 1} \right).$$

A consideration of the limiting wave lengths gives still another way of expressing these formulae. If they are written in wave numbers their differences are seen to be constant.

$$10^8/\lambda_0 = 25227, 24366.5, 23506$$

with the constant difference 860.5. Therefore $\lambda_0^{-1} = A + Bn$ where n takes integral values. Substituting values for this and rearranging it, the following formula for the Balmer series in the Wolf-Rayet stars is obtained:

$$\lambda = \frac{2\lambda_0}{1 + nd} \left(\frac{m^2}{m^2 - q^2/4\omega^2} \text{ or } \frac{m^2}{m^2 - 1} \right)$$

in which $\lambda_0 = 5007$, the principal wave length of the neutral atom of nebium, n takes successive integral values, and $d = 0.08609$ and is not arbitrary, but is calculated from data involved in the consideration of the neutral nebium atom.

The above equation is one of the most remarkable and important points of Nicholson's work, for in it he succeeds in bringing together the simple ring systems which are not known on the earth, and our ordinary elements.

It is evident that a change in the term n means a change of some sort in the atom. It is also evident that it must be of a character that the force between the component parts does not change. It seems inevitable that the change must consist in a change in the nucleus, which does not alter its charge. It is significant that the simple ring systems seem to be incapable of giving rise to Balmer series, and the only logical conclusion is that they depend on the intimate structure of the nucleus. The elements which give rise to Balmer series may then be looked upon as the evolution products of the simple ring system on which the value of λ_0 depends. This is considering λ_0 as belonging to any simple ring system and not to nebulium alone.

Nicholson shows that the simple ring system $1e$ can have only one vibration frequency, $q = \omega$. This has already been calculated as $\lambda = 1823.35$, which is exactly one-half of the limiting wave length of the Balmer series for hydrogen. From the formula

$$\lambda = \frac{2\lambda_0}{1 + nd} \left(\frac{m^2}{m^2 - 4} \right),$$

it is seen that, to derive the hydrogen Balmer formula, n must be equal to 0. That is, hydrogen would appear to be the first evolution product of the system $1e$, protohydrogen.

It should be noted that Nicholson has in a rather round-about way succeeded in evaluating the Rydberg constant even more closely than did Bohr. He has not, however, attempted to give any physical picture of the mechanism of the production of the Balmer series.

While up to the present time the evolution products of the other systems are not known in general, it is likely that they may be some of our terrestrial elements. The lines due to a number of the evolution products of nebulium are shown in the Wolf-Rayet stars.

No work has yet been published connecting helium with the simple ring systems, although from the fact that it appears in the nebulae and the stars about the same time as does hydrogen, it seemed likely that it is one of the early evolution products of one of the systems. In some work as yet unpublished Nicholson has succeeded in showing that helium is the evolution product of the system $2e$.

From the progressive changes of the spectra of the stars, and other evidence which points to their age, it seems likely that all of our common elements are more complex forms of matter than the simple ring systems and hydrogen, and are built up from them. In such spectra the elements make their appearance in the order of their atomic weights.

According to Nicholson's idea, then, our ordinary terrestrial elements are evolution products of the simple ring systems found in the nebulae and the stars. That is, they have nuclei which are complex, containing both positive and negative electrons. This is in good accord with other facts but it does not agree with Rutherford's idea that the nucleus of the hydrogen atom may be the positive electron. If the astronomical evidence is admitted, it may be safely assumed that in the novae and nebulae, where the temperature is supposed by Nicholson to be very high, the complex atoms are unstable, breaking up into simple ones, or if the process is looked at from the other point of view, as these hot bodies cool the simple ring systems condense, becoming more complex and giving rise to the elements known on the earth.

The only very important papers on atomic structure which have not been considered are those of Stark. His work has been omitted on account of lack of space, and because he has not as yet been able to obtain from his results any very definite picture of the structure of the atom. Another reason is that this work is already available in book form³¹ which is not true of the material presented in this paper. Stark's greatest discovery is that of the electrical Zeeman effect, or the Stark effect, which is the decomposition of the spectral lines by means of a static electrical charge. Up to the present time this effect, which has been made to give a much greater separation of the components of the lines than has been obtained by the Zeeman effect, has been obtained only in the spectra from canal or positive rays. However this is probably due to the fact that this is the only method which has been found for securing the high field strengths which are essential. In Stark's work he has used a potential fall of from ten to seventy-four thousand volts per centimeter.

BIBLIOGRAPHY.

1. Kelvin, *Phil. Mag.*, **3**, 257 (1902).
2. Rutherford, *Ibid.*, **21**, 669 (1911).
3. Geiger and Marsden, *Proc. Roy. Soc.*, **82A**, 495 (1909).
4. Geiger, *Ibid.*, **83**, 492 (1910).
5. Geiger, *Proc. Man. Lit. and Phil. Soc.*, **55**, pt. II, 20 (1913); *Phil. Mag.*, **5**, 604 (1913).
6. Nagaoka, *Phil. Mag.*, **7**, 445 (1904).
7. Rutherford and Nuttal, *Ibid.*, **26**, 702 (1913).
8. Marsden, *Ibid.*, **27**, 824 (1914).
9. Rutherford, *Ibid.*, **27**, 448 (1914).
10. Barkla, *Ibid.*, **21**, 648 (1911).
11. van den Broek, *Physik. Z.*, **14**, 33 (1913).
12. Bohr, *Phil. Mag.*, **26**, 1 (1913).
13. Moseley, *Ibid.*, **26**, 1024 (1913); **27**, 703 (1914).
14. Laue, *Ann. Physik*, **41**, 989 (1913).
15. Bragg and Bragg, *Proc. Roy. Soc.*, **88A**, 428 (1913); *Ibid.*, **89A**, 246 (1914).
16. Barkla and Sadler, *Phil. Mag.*, **16**, 550 (1908).
17. Aston, *Eng.*, **96**, 423 (1913).

18. Russell and Ross, *Proc. Roy. Soc.*, **87A**, 478 (1912).
 19. Exner and Haschek, *Sitzb. K. Akad. Wiss. Wien.*, **121**, 175 (1912).
 20. Soddy, *Chem. News*, **107**, 97 (1913).
 21. Fajans, *Ber.*, **46**, 422 (1913).
 22. Rutherford and Andrade, *Phil. Mag.*, **27**, 867 (1914).
 23. Richards, *THIS JOURNAL*, **36**, 1329 (1914).
 24. Soddy, *J. Chem. Soc.*, **105**, 1402 (1914); Curie, *Compt. rend.*, **158**, 1676 (1914).
 25. Soddy, *Nature*, **94**, 615 (1915).
 26. Bohr, *Phil. Mag.*, **26**, 476, 857 (1913).
 27. Evans, *Ibid.*, **29**, 284 (1915).
 28. Bohr, *Ibid.*, **29**, 332 (1915).
 29. Nicholson, *Ibid.*, **27**, 541 (1914); **28**, 90 (1914).
 30. Nicholson, *Mon. Not. Roy. Ast. Soc.*, **72**, 49 (1911); **72**, 139 (1911); **72**, 677 (1912); **72**, 729 (1912); **73**, 382 (1912); **74**, 118 (1913); **74**, 204 (1913); **74**, 425 (1913); **74**, 486 (1914); **74**, 623 (1914).
 31. Stark, "Die elektrischen Quanten," S. Hirzel, Leipzig (1910); "Die elementare Strahlung," S. Hirzel, Leipzig (1911); "Elektrische Spektralanalyse chemischer Atome," S. Hirzel, Leipzig (1914). Contains a bibliography. J. J. Thomson, "The Forces between Atoms and Chemical Affinity," *Phil. Mag.*, **27**, 757 (1914); Rutherford and Robinson, *Ibid.*, **26**, 342, 937 (1913); Darwin, "The Theory of X-ray Reflection," *Ibid.*, **27**, 315, 675 (1914); Hicks, "Effect of the Magnetron in the Scattering of X-rays," *Proc. Roy. Soc.*, **90A**, 356 (1915); van den Broek, "On Nuclear Electrons," *Phil. Mag.*, **27**, 455 (1914); J. H. Jeans, "Report on Radiation and the Quantum Theory to the Physical Society of London" (1914); Fowler, "The Pickering Series Spectrum," Bakerian Lecture, 1914; *Phil. Trans. A.*, **214**; *Proc. Roy. Soc.*, **90A**, 426 (1915); Crehore, "Theory of Atomic Structure," *Phil. Mag.*, **29**, 310 (1915).
- X-ray spectra: Bragg, W. H., *Nature*, **91**, 477 (1912); Bragg, W. H. and W. L., *Proc. Roy. Soc.*, **88A**, 426 (1913); Bragg, W. L., *Phil. Mag.*, **28**, 355 (1914); Bragg, W. H., *Eng.*, **97**, 814 (1914); Bragg, W. L., *Proc. Roy. Soc.*, **89A**, 241 (1914); *Ibid.*, **89A**, 248 (1914); Bragg, W. H. and W. L., *Ibid.*, **89A**, 277 (1914); Bragg, W. H., *Ibid.*, **89A**, 430 (1914); Bragg, W. L., *Ibid.*, **89A**, 468 (1914); Bragg, W. H., *Ibid.*, **89A**, 575 (1914).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THROOP COLLEGE OF TECHNOLOGY.]

OSMOTIC PRESSURE AND CONCENTRATION IN SOLUTIONS OF ELECTROLYTES, AND THE CALCULATION OF THE DEGREE OF IONIZATION.

By STUART J. BATES.

Received March 17, 1915.

1. Introduction.

Ostwald's dilution law, which is obtained by the application of the law of mass action to solutions of electrolytes, involves the concentration of the ions and that of the undissociated molecules. The large divergence from this law which strong electrolytes exhibit may hence be due to the behavior of the ions, to that of the undissociated molecules, or to that of both. This so-called anomalous behavior may be simply expressed by saying that for one or for both of these molecular species van't Hoff's law,

$\pi V = RT^1$ does not hold, for if all of the molecular species entering into an equilibrium obey this law, the law of mass action is a thermodynamic necessity.²

It is the purpose of this paper to develop and apply methods for determining the numerical relation which holds, in the place of that given by van't Hoff's law, between the osmotic pressure of the ions and their concentration, and the similar relation for the undissociated molecules. The divergence from the law of mass action may hence be split up into two distinct parts which may to a great extent be studied separately. The calculations will be based upon the commonly accepted assumption that the degree of ionization may be determined from conductance and viscosity data. Other assumptions which may be employed as a basis upon which to calculate the degree of ionization, for example, the assumption that the ions are normal, that is that van't Hoff's law is obeyed, will be considered and the conclusions to which they lead with respect to the behavior of the solute discussed.

Data which may be used for the calculation of the relation between osmotic pressure and concentration are conductance³ measurements, together with determinations of one of the colligative properties such as osmotic pressure, freezing-point lowering, electromotive force of concentration cells, etc. It will not be necessary to introduce, in order to carry out these calculations, any assumptions other than those already generally accepted. In addition to those of thermodynamics these are (1) that in dilute solutions of a di-ionic electrolyte the osmotic pressure due to each of the two ions is the same, and (2) that the degree of ionization (γ) is given by the conductance-viscosity ratio, the concentration of each ion being $C\gamma$ and that of the undissociated molecules $C(1 - \gamma)$. These assumptions are discussed below, where it is shown that the most reliable data support them and can be best interpreted by their aid.

There is a choice of systems to be used in discussing the properties of solutions. Any one, of vapor pressure, osmotic pressure, thermodynamic potential, activity, etc., may be employed. None of these possesses a theoretical advantage over the others, for all must involve the same assumptions or experimental data, and all lead to the same conclusions. Osmotic pressure is used here because it may be readily visualized, because of its general use among chemists and because of the relative simplicity of its thermodynamic treatment. The results may, of course, be readily "translated" into one of the other "languages," that of activity, for example. Mols per unit volume of solution is the most suit-

¹ π = osmotic pressure, V = volume containing one mol of solute, R = gas constant, T = absolute temperature.

² Washburn, *THIS JOURNAL*, 32, 485 (1910).

³ Whenever possible the conductance data should be corrected for viscosity.

able unit of concentration to employ since then the quotient, osmotic pressure divided by concentration, has the dimensions of energy and may be readily introduced into thermodynamic relations.

2. The Method of Calculation.

Outline of the Method.—If it be assumed that, in a solution of a di-ionic electrolyte, the osmotic pressure due to one of the ions is equal to that due to the other, then thermodynamics yield for equilibrium in solution the rigorous relation,¹

$$\frac{2d\pi_i}{C_i} - \frac{d\pi_u}{C_u} = 0 \quad (1)$$

where π_i and π_u are the osmotic pressures due to the ions at the concentration C_i and the undissociated molecules at the concentration C_u , respectively. By the aid of the same assumption the relation

$$\pi = 2\pi_i + \pi_u, \quad (2)$$

follows, *i. e.*, the total osmotic pressure (π) of the solution is the sum of two effects, one the osmotic pressure of the ions, the other that of the undissociated molecules. If now C_i and C_u are calculated from conductance data, and if the total osmotic pressure of the solution be known (either from direct measurements or from freezing-point determinations), it is possible to determine for any concentration interval for which data are available the relation between π_i and C_i and the relation between π_u and C_u , for there are two equations and but the two unknown quantities π_i and π_u . The fact that one of the equations is a differential equation makes their solution somewhat lengthy, but none the less rigorous.

The methods of performing these calculations are necessarily somewhat complicated. The remainder of this section gives in detail and with an example, mathematical methods which have been found convenient for solving the above equations; it may be omitted by readers not particularly interested in these methods. The assumptions involved and the conclusions to be derived are discussed in nonmathematical terms in the following sections.

Calculation of Osmotic Pressure from Freezing-point Data.—There are very few accurate direct measurements of the osmotic pressures of aqueous solutions of electrolytes. However, many careful determinations have been made of the freezing-point lowerings (Δt_f) of such solutions. From the resulting data, the osmotic pressures of these solutions may be readily and accurately calculated by means of the following equation:²

$$\pi = 12.06(\Delta t_f - 1.78 \cdot 10^{-3} \Delta t_f^2 - 2.5 \cdot 10^{-6} \Delta t_f^3) \quad (3)$$

¹ See Washburn, *THIS JOURNAL*, 32, 484 (1910).

² Washburn, *Ibid.*, 32, 499 (1910).

Thus the osmotic pressure of the solute¹ at the freezing point of the solution may be computed. It is most convenient to compare the osmotic pressures at the common temperature 0° . The temperature correction may be calculated from the Helmholtz equation

$$d\pi = (\pi - q) dT/T,$$

where q is the heat evolved on adding unit volume of solvent to an infinitely large amount of the solution. In general, the error which is involved in assuming $q = 0$, is smaller than is the probable error of the freezing-point determinations.² The temperature correction may hence be taken as

$$\Delta\pi = \pi \Delta t_f / 273.1$$

and by combining this relation with Equation 3 we have for the osmotic pressure at 0° the equation

$$\pi = 12.06(1 + 0.00188 \Delta t_f) \Delta t_f. \quad (4)$$

This equation gives within a few hundredths of one per cent. the osmotic pressure at 0° of solutions as concentrated as $0.2 N$ and within 0.2 or 0.3% that for solutions up to $0.5 N$.

Solution of the Equations.—The differential Equation 1 may be written thus:³

$$2(1 - \gamma)d\pi_i - \gamma d\pi_u = 0. \quad (5)$$

By differentiating Equation 2, multiplying through by γ and adding the result to (5) we get

$$d\pi_i = \gamma/2 d\pi. \quad (6)$$

Now since from differential calculus

$$d\left(\frac{\pi}{C_i}\right) = \frac{C_i d\pi - \pi dC_i}{C_i^2} \quad (7)$$

hence

$$\frac{d\pi}{dC_i} = \frac{\pi}{C} + \frac{d(\pi/C_i)}{d \ln C_i} \quad (7a)$$

and from (6)

$$\frac{d\pi_i}{dC_i} = \frac{\gamma}{2} \frac{d\pi}{dC_i} = \frac{\gamma}{2} \left[\frac{\pi}{C_i} + \frac{d(\pi/C_i)}{d \ln C_i} \right] = \frac{1}{2} \left[\frac{\pi}{C} + \frac{\gamma}{2.303} \frac{d(\pi/C_i)}{d \log C_i} \right]. \quad (8)$$

¹ As derived by Washburn the osmotic pressure in Equation 3 is that of the solvent. However, by employing the Duhem relation $N_w V_w d\pi_w + N_s V_s d\pi_s = 0$, and the fact that $N_w V_w = N_s V_s$ the osmotic pressure of the solute may be substituted for that of the solvent (water) in the original differential equation and in those which follow.

² In the case of the common salts whose heats of dilution have been determined by Rumelin, *Z. physik. Chem.*, **58**, 449 (1907); Bishop, *Phys. Rev.*, **26**, 169 (1904) or Magie, *Ibid.*, **35**, 265, 272 (1912) the error for solutions more dilute than $0.2 N$ is less than 0.05% .

³ γ = degree of ionization.

This is the equation used for determining $d\pi_i/dC_i$, i. e., the rate of change of the osmotic pressure of the ions with their concentration. The ratio π/C in Equation 8 may of course be calculated directly from the data. The term,

$$\frac{\gamma}{2.303} \frac{d(\pi/C_i)}{d \log C_i},$$

which is small in comparison with the other, may be readily determined by either of two methods. Values of π/C_i may be plotted against those of $\log C_i$ and tangents to the curve graphically determined, or the obvious algebraic method may be employed. Having determined $d\pi_i/dC_i$ for a number of concentrations, values of π_i/C_i may be determined by integration, either graphic or algebraic.

In order to determine the similar ratios for the undissociated molecules, a procedure similar to the above might be employed. In practice, however, it is more convenient to use a different method. By eliminating K , C_i , and C_u from Storch's equation [$C_i^n/C_u = K$] from the differential equation derived from this, (C_i and C_u being taken as the variables) and from Equation 1, the relation

$$\frac{d\pi_u}{dC_u} = \frac{2}{n} \frac{d\pi_i}{dC_i} \quad (9)$$

is obtained. That is, having determined $d\pi_i/dC_i$ and values for n^1 over any given concentration range, it is possible to calculate $d\pi_u/dC_u$ and hence by integration to determine the osmotic pressure of the undissociated molecules as a function of their concentration.

Calculation of Osmotic Pressure from Electromotive Force Measurements.—For the electromotive force (E) of a concentration cell with electrodes reversible to the cation and involving transference, thermodynamics gives the equation²

$$FdE = N_a[V_c d\pi_c + V_a d\pi_a]. \quad (10)$$

Here F is the faraday, N_a the Hittorf transference number of the anion,³ V_c and V_a the volumes containing one mol of the cation and anion, respectively, and π_c and π_a the osmotic pressures of the cation and anion, respectively. If it be assumed that the two ions behave in a similar manner as regards their osmotic pressure, then, writing $1/C_i$ for V_c and for V_a , the following relation results:

$$dE = \frac{2N_a}{F} \frac{d\pi_i}{C_i} \quad (10a)$$

Hence,

¹ It has been shown that n changes with the concentration and methods for determining this exponent have been developed. Bates, *THIS JOURNAL*, 35, 519 (1913).

² Washburn, *THIS JOURNAL*, 32, 495 (1910).

³ For cells involving no transference, N should be replaced by unity.

$$\frac{d\pi_i}{dC_i} = \frac{F}{2N_a} \frac{dE}{d \ln C_i} \quad (11)$$

By transformations similar to those employed above (Equations 7 and 7a), the following may be obtained:

$$\frac{dE}{d \ln C_i} = \frac{E}{\ln C_i} + \ln C_i \frac{d(E/\ln C_i)}{d \ln C_i}.$$

Hence, from Equation 11

$$\frac{d\pi_i}{dC_i} = \frac{F}{2N_a} \cdot \frac{1}{2.303} \left[\frac{E}{\log C_i} + \log C_i \frac{d(E/\log C_i)}{d \log C_i} \right] \quad (12)$$

By plotting values of $E/\log C_i$ against those of $\log C_i$, $\frac{d(E/\log C_i)}{d \log C_i}$ at any concentration may be determined, and hence, by means of Equation 12 $d\pi_i/dC_i$ may be computed. The calculation of π_i/C_i , of $d\pi_u/dC_u$ and of π_u/C_u is then exactly similar to that indicated in the discussion of the freezing-point data.

Example.—There is a much greater supply of accurate data concerning the freezing-point lowering of solutions available, than there is of that with regard to the electromotive force of concentration cells. The application of the above methods will hence be illustrated for the former kind of data only.

Table I gives the details of this calculation for solutions of potassium chloride. In the first column is given the concentration in equivalents per liter (C), in the second the corresponding value of the freezing-point lowering divided by the concentration in mols per 1000 grams of water. From 0.001 *N* to 0.05 *N* these values were interpolated by Flügel from his own excellent measurements.¹ The value given by him for 0.1 *N* (the most concentrated solution which he investigated) does not agree very well with his values for the more dilute solutions, neither does it agree with the careful measurements of Jahn,² Loomis³ or Barnes.⁴ Hence for this concentration the value in Column II is the mean of Flügel's value and that given in the compilation of Noyes and Falk⁵ as the best value. For the higher concentrations the data is taken from the compilation of Noyes and Falk. It is based largely upon the work of Jahn, of Loomis and of Barnes.

Employing the density data of Freund,⁶ values of $\Delta t_f/C$ were next calculated and then by the aid of Equation 4 values of $\pi/C \div RT$, these are

¹ *Z. physik. Chem.*, 79, 583 (1912).

² *Ibid.*, 50, 129 (1904); 59, 31 (1907).

³ *Wied. Ann.*, 57, 495 (1896).

⁴ *Trans. Nova Scotian Inst. of Science*, 10, 153.

⁵ *THIS JOURNAL*, 32, 1011 (1910).

⁶ *Z. physik. Chem.*, 66, 580 (1909).

given in Column III. By dividing these by the degrees of dissociation,¹ values of $\pi/C_i \div RT$ were obtained, which were then plotted against values of $\log C_i$, the tangents $\frac{d(\pi/C_i) \div RT}{d \log C_i}$ given in Column V were determined from this curve. Values of $d\pi_i/dC_i \div RT$ were then calculated by means of Equation 8. The figures for n were calculated from conductance data and were used to compute values of $d\pi_u/dC_u \div RT$ by means of Equation 9.

In order to integrate the coefficients in Columns VI and VIII, values of $\log (1 - d\pi_i/dC_i \div RT)$ were plotted against values of $\log C_i$, and those of $\log (d\pi_u/dC_u \div RT - 1)$ against values of $\log C_u$. The curves which

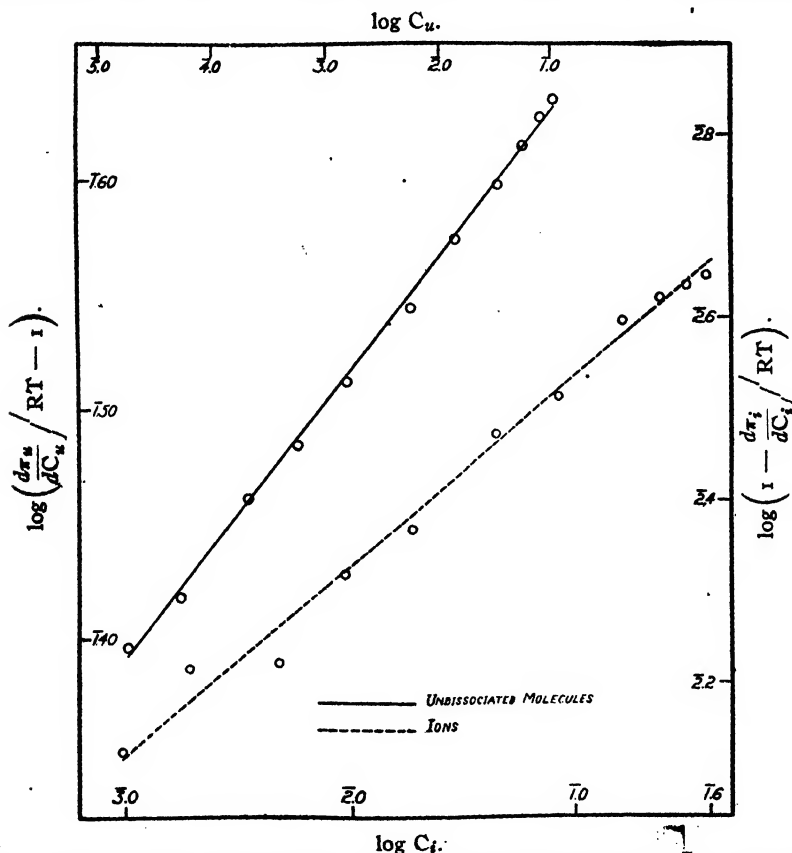


Fig. 1.—The Osmotic Pressure-Concentration Relations of the Ions and of the Undissociated Molecules of Potassium Chloride.

¹ Within the experimental error, the degrees of ionization of potassium chloride solutions of the same concentration are the same at 0° and at 18°. Since the conductivity data at the higher temperature is much more consistent with itself, the degrees of ionization calculated for 18° have been used in the present computations.

are given in Fig. 1 are straight lines. For the ions the greatest percentage deviation from the linear relation is 0.15%, that for the undissociated molecules is 0.30%. These are well within the experimental error of the freezing-point determinations. The equation for one line is

$$\log (1 - d\pi_i/dC_i \div RT) = 0.207 \log C_i - 0.258,$$

hence,

$$d\pi_i/dC_i \div RT = 1 - 0.0552 C_i^{0.207}$$

and integrating

$$\pi_i/C_i \div RT = 1 - 0.0457 C_i^{0.207}. \quad (13)$$

In a similar way the equation

$$\pi_u/C_u \div RT = 1 + 0.464 C_u^{0.0632} \quad (13a)$$

was obtained.

From these equations, values of $\pi_i/C_i \div RT$ and of $\pi_u/C_u \div RT$ were calculated; these are given in Columns IX and X. The osmotic pressures of the ions and of the undissociated molecules were then calculated at each concentration, these added together and divided by the concentration, giving the figures in Column XI. The percentage difference between the values thus calculated and those observed (Column III) are given in the last column. It is evident that the above numerical equations express the data very exactly. The greatest percentage difference, that at 0.001 *N*, corresponds to an error in the freezing-point determination of 0.00001°, the next largest, that at 0.2 *N* to an error of less than 0.0015°.

3. Results of the Calculation.

The results of calculations based on freezing-point data¹ for a number of representative di-ionic² electrolytes are given in Table II. They are given as ratios such as $d\pi_i/dC_i \div RT$, that is as deviations from van't

¹ The data for the dilute solutions of potassium chloride, of sodium chloride and of sodium chlorate are due to Flügel (*Loc. cit.*) at the higher concentrations in these cases and in others the "best" values given in the compilation of Noyes and Falk (*Loc. cit.*) were employed. For potassium nitrate up to and including 0.1 *N* the data of Adams (*THIS JOURNAL*, 37, 481 (1915)) were employed, above 0.1 *N* those of Roth were used. The calculations in the case of sodium nitrate are based in part on the results of Loomis (*Wied. Ann.*, 57, 495 (1896)) but chiefly upon those of Roth (*Z. physik. Chem.*, 79, 599 (1912)). For cesium nitrate the determinations of Biltz and Meyer (*Ibid.*, 40, 218 (1912)), of Washburn and MacInnes (*THIS JOURNAL*, 33, 1686 (1911)) and of Roth were interpolated. In the case of lithium chloride the results of Jahn (*Z. physik. Chem.*, 50, 129 (1904); 59, 31 (1907)) and of Washburn and MacInnes were employed. For the most dilute solutions of copper sulfate and of magnesium sulfate the data of Hausrath (*Ann. phys.*, [4] 9, 522 (1902)) and of Bedford (*Proc. Royal Soc.*, 83A, 454 (1910)) were interpolated, for the moderately concentrated solutions the "best" values of Noyes and Falk were used.

² The probable presence of complex ions makes the application of the above methods to salts of higher type impossible without the introduction of simplifying assumptions.

Hoff's law simply as a matter of convenience and comparison. The terms normal and abnormal, meaning agreement with or deviation from the requirements of this law or from proportionality between activity and concentration, are employed throughout this paper because they are in general use and because they offer a convenient means of discussing the results. These terms are, however, somewhat misleading for they appear to indicate a certain necessary or at least expected behavior or relation.

The values show the manner in which the osmotic pressure of the ions and that of the undissociated molecules changes with their respective concentrations. For most purposes the rate of change with the concentration, *i. e.*, $d\pi_i/dC_i$ or $d\pi_u/dC_u$ is more useful than the integrated ratio π_i/C_i or π_u/C_u . It is the differential coefficient, not the fraction π/C , which is introduced into thermodynamic relations in order to drive the mass law, the Nernst equation, etc. Further, the differential ratio gives more accurate information regarding the properties of the solution at any given concentration than does the integrated ratio. The value of the former depends only upon the properties of the solution at the concentration in question, while that of the latter is influenced by and to a great extent depends upon the properties of the solutions of all concentrations from the infinitely dilute solution up to that in question. For example, the molecular freezing-point lowering has been used in discussing the degree of hydration of solutes at various concentrations. The more logical value to use, if such a method is applicable to the problem, is the rate of change of the molecular freezing-point lowering with the concentration.

The uncertainties in the values given for $d\pi_i/dC_i$ largely depend upon those of the freezing-point data, since they are but slightly influenced by errors in the conductance measurements.¹ The figures for potassium chloride, sodium chloride and sodium chlorate, the freezing-point lowerings of whose solutions was determined by Flügel, are probably accurate to a few tenths of one per cent. The errors in the case of the other salts are somewhat larger.

The uncertainty in the values for $d\pi_u/dC_u$ is considerably greater than that in the similar ratio for the ions. It depends largely upon the reliance which may be placed upon the conductance data and upon the value chosen for the equivalent conductance at infinite dilution (Λ_0). This follows from the fact that the calculation of the ratios involves values of n , which, particularly at low concentrations, are very sensitive to irregularities in conductance data and to errors in the value of Λ_0 . Thus, for potassium chloride a change of 0.05% in Λ_0 becomes one of about 1% in the differential ratio at 0.001 *N*.²

¹ It follows from the form of Equation 8 that the values determined for the above differential ratio are not affected by errors in the value chosen for the equivalent conductance at infinite dilution.

² See also Table II. *THIS JOURNAL*, 35, 526 (1913).

If the values for Λ_0 which were calculated by Kohlrausch are used, values are obtained for $d\pi_u/dC_u$ such that the deviation from van't Hoff's law is a minimum at about 0.002 N and that at lower concentrations the abnormality becomes greater. Other objections against such values have been presented.¹ Kraus and Bray,² as a result of a very thorough and extensive study of conductance data, rejected Kohlrausch's data for solutions more dilute than 0.001 N and chose an unusually small value for Λ_0 . If their view is correct the deviations of the undissociated molecules, particularly below 0.01 N , are much less than those given in Table II. The present author finds, however, that, at least in the case of potassium chloride, Kohlrausch's data from 1.0 N to 0.0001 N may be represented by an empirical equation, somewhat similar to that of Kraus, with an average deviation of but 0.03%.³ Hence, using the same type of argument as that employed by Kraus and Bray, the data within this range are accurate, and the Λ_0 value consistent with this equation is the most probable one. The value thus given is within 0.05% of that previously chosen by means of two different and independent methods.⁴ It is believed that the uncertainty in the values for $d\pi_u/dC_u \div RT$ due to errors in the conductance data or in the Λ_0 values is, in general, less than 1%.

The values of Table II show that, even in solutions as dilute as 0.001 N , neither the ions nor the undissociated molecules obey van't Hoff's law, though with decreasing concentration both become more nearly normal.

Behavior of the Ions.—The osmotic pressure of the ions is less than that calculated from this law. This is true in every case except for solutions of lithium chloride 0.1 N and above; hydration is evidently the cause of this exception. The behavior of the ions may be represented within the error of the freezing-point determinations by an equation of the form

$$d\pi_i/dC_i = RT (1 + kC_i^m). \quad (14)$$

As is to be expected, the greater the hydration of the salt and the higher the concentration, the greater the deviation from this relation. In all cases where a regular deviation occurs at high concentrations it is in the direction predicted by hydration effects, and it is least for the slightly hydrated salts. In Table III are given for each of the salts (except lithium chloride) values of the constants k and m which fit the data. The average of the percentage deviations which are irregularly distributed⁵ is given for each salt in the last column of Table III. These deviations

¹ Bates, *THIS JOURNAL*, 35, 519 (1913).

² *THIS JOURNAL*, 35, 1315 (1913).

³ A more extended discussion of conductance data is reserved for a future communication.

⁴ Bates, *THIS JOURNAL*, 35, 532 (1913).

⁵ See for example the figure for potassium chloride.

TABLE II.—OSMOTIC PRESSURE OF THE IONS AND OF THE UNDISSOCIATED MOLECULES CALCULATED FROM FREEZING-POINT DATA.

| Equiv. per liter. | KCl. | | NaCl. | | NaClO ₄ . | | LiCl. | | NaNO ₃ . | |
|----------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| | $\frac{d\pi_i/dC_i}{Rt}$ | $\frac{d\pi_u/dC_u}{RT}$ | $\frac{d\pi_i/dC_i}{RT}$ | $\frac{d\pi_u/dC_u}{RT}$ | $\frac{d\pi_i/dC_i}{RT}$ | $\frac{d\pi_u/dC_u}{RT}$ | $\frac{d\pi_i/dC_i}{RT}$ | $\frac{d\pi_u/dC_u}{RT}$ | $\frac{d\pi_i/dC_i}{RT}$ | $\frac{d\pi_u/dC_u}{RT}$ |
| 0.001 | 0.9866 | 1.249 | 0.9960 | 1.263 | 0.9960 | 1.285 | ... | ... | .. | ... |
| 0.002 | 0.9835 | 1.262 | 0.9933 | 1.280 | 0.9933 | 1.309 | ... | ... | .. | ... |
| 0.005 | 0.9833 | 1.289 | 0.9897 | 1.305 | 0.9870 | 1.325 | 0.998 ¹ | 1.338 ¹ | .. | ... |
| 0.01 | 0.9791 | 1.305 | 0.9862 | 1.323 | 0.9830 | 1.331 | 0.985 | 1.334 | .. | ... |
| 0.02 | 0.9766 | 1.325 | 0.9826 | 1.343 | 0.9813 | 1.331 | 0.993 | 1.366 | 0.9746 ² | 1.310 ³ |
| 0.05 | 0.9703 | 1.350 | 0.9804 | 1.375 | 0.9807 | 1.323 | 0.986 | 1.390 | 0.9683 | 1.311 |
| 0.1 | 0.9673 | 1.375 | 0.9728 | 1.394 | 0.989 | 1.325 | 1.000 | 1.439 | 0.9563 | 1.301 |
| 0.2 | 0.9605 | 1.396 | 0.9630 | 1.413 | .. | ... | 1.015 | 1.500 | 0.9482 | 1.296 |
| 0.3 | 0.9581 | 1.412 | 0.9652 | 1.446 | .. | ... | 1.046 | 1.577 | 0.9400 | 1.287 |
| 0.5 | 0.9557 | 1.432 | 0.9675 | 1.488 | .. | ... | 1.110 | 1.728 | .. | ... |

¹ Concentration = 0.006.² Concentration = 0.025.

| Equiv. per liter. | KNO ₃ | | CsNO ₃ | | CuSO ₄ | | MgSO ₄ | |
|----------------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| | $\frac{d\pi_i/dC_i}{RT}$ | $\frac{d\pi_u/dC_u}{RT}$ | $\frac{d\pi_i/dC_i}{RT}$ | $\frac{d\pi_u/dC_u}{RT}$ | $\frac{2d\pi_i/dC_i}{RT}$ | $\frac{2d\pi_u/dC_u}{RT}$ | $\frac{2d\pi_i/dC_i}{RT}$ | $\frac{2d\pi_u/dC_u}{RT}$ |
| 0.001 | .. | ... | ... | ... | 0.927 | 1.090 | 0.936 | 1.114 |
| 0.002 | .. | ... | ... | ... | 0.919 | 1.091 | 0.935 | 1.126 |
| 0.005 | 0.9900 | 1.279 | ... | ... | 0.899 | 1.085 | 0.923 | 1.136 |
| 0.01 | 0.9830 | 1.281 | ... | ... | 0.867 | 1.067 | 0.900 | 1.136 |
| 0.02 | 0.9719 | 1.275 | 0.963 | 1.242 | 0.824 | 1.046 | 0.857 | 1.118 |
| 0.05 | 0.9464 | 1.246 | 0.953 | 1.202 | 0.756 | 1.025 | 0.778 | 1.073 |
| 0.1 | 0.9260 | 1.217 | 0.932 | 1.151 | 0.734 | 1.055 | 0.705 | 1.030 |
| 0.2 | 0.888 | 1.159 | 0.892 | 1.100 | ... | ... | ... | ... |
| 0.3 | 0.850 | 1.100 | 0.877 | 1.070 | ... | ... | ... | ... |

are the averages obtained by applying Equation 14 to the entire concentration range, except in the cases of sodium chloride and of sodium chlorate; in the former case the equation does not show good agreement above 0.2 *N* and in the latter above 0.05 *N*.

TABLE III.—APPLICATION OF EQUATION 14 TO THE BEHAVIOR OF IONS.

| Electrolyte | KCl | NaCl | NaClO ₃ | NaNO ₃ | KNO ₃ | CsNO ₃ | CuSO ₄ | MgSO ₄ |
|-------------|---------|---------|--------------------|-------------------|------------------|-------------------|-------------------|-------------------|
| <i>k</i> | —0.0552 | —0.0690 | —0.0580 | —0.1055 | —0.400 | —0.295 | —0.730 | —0.836 |
| <i>m</i> | 0.207 | 0.376 | 0.320 | 0.377 | 0.660 | 0.542 | 0.407 | 0.483 |
| Av. % diff. | 0.08 | 0.11 | 0.25 | 0.08 | 0.20 | 0.5 | 1.1 | 1.0 |

The results given in Table II for copper sulfate and for magnesium sulfate show, not only that the osmotic pressure of the doubly charged ion is less than that calculated from van't Hoff's law, but also that it is much less than that determined for univalent ions at the same concentration. This result, expressed in terms of activity, has been pointed out by Lewis and Lacey,¹ who measured the electromotive force of copper sulfate concentration cells. Their experimental results indicate a deviation even greater than that calculated from freezing-point data.

In order to carry out the above calculations it is necessary to assume that the osmotic pressures of the two ions in a solution of a di-ionic electrolyte are the same. If such an assumption is not made it is apparently impossible with our present methods to solve the main problems connected with the theory of solutions. Otherwise the variables are too numerous for the number of independent experimental methods as yet developed. The results warrant the conclusion that up to moderate concentrations the assumption is justified. At concentrations below 0.05 *N* the behavior of the chloride ion, as calculated from the data for potassium chloride agrees within the experimental error with that derived from sodium chloride. The behavior of the sodium ion is the same whether calculated from the data for sodium chloride or for sodium chlorate. For the nitrate ion the data for potassium nitrate give the same results as the data for sodium nitrate and for cesium nitrate. The data for copper sulfate and for magnesium sulfate give agreeing results for the sulfate ion.

At higher concentrations hydration has an effect upon the osmotic pressure of the various constituents of the solutions, and since the degree of hydration varies from salt to salt the same agreement is not to be expected in concentrated solutions. As to whether or not hydration has the same influence upon the osmotic pressure of both ions it is impossible to judge from the present calculations.

Behavior of the Undissociated Molecules.—The undissociated molecules have an osmotic pressure considerably greater than that calculated from van't Hoff's law. At moderate concentrations the salts do not be-

¹ THIS JOURNAL, 36, 804 (1914).

have similarly. In the case of the chlorides the deviations continue to increase with the concentration, for the nitrates a maximum is reached about $0.02 N$. This somewhat surprising result, that the behavior of the least hydrated is the most complex is connected with the fact that the exponent n is for these salts a minimum at about $0.02 N$.

Since n may be calculated from conductance data alone, and since the deviation in the case of the ions is relatively small and may be extrapolated to more dilute solutions with a considerable degree of accuracy, hence values of $d\pi_u/dC_u \div RT$ may be calculated to within 1 or 2% for solutions more dilute than those for which freezing-point data are available. In this way it may be shown that in solutions more dilute than $0.01 N$ the undissociated molecules of the various uni-univalent salts behave in practically the same manner and that at $0.0001 N$ the deviation from van't Hoff's law is still about 15%.

For solutions more dilute than $0.01 N$ an empirical equation, of a form similar to that which holds for the ions, expresses the relation between the osmotic pressure of the undissociated molecules and their concentration. In the cases of potassium chloride¹ and of sodium chloride the equation has a considerably greater range.

The behaviors of the undissociated molecules of copper sulfate and of magnesium sulfate are remarkable in two particulars. First they show an almost constant deviation from van't Hoff's law from $0.001 N$ to $0.02 N$. In the second place they obey this law much more closely than do the undissociated molecules of uni-univalent salts, in fact above $0.01 N$ they are more nearly normal than are the ions into which they dissociate.

Effect of Hydration.—Hydration is usually considered to increase the osmotic pressure or the freezing-point lowering of a solution largely by lessening the amount of "free" water in the solution. Table II shows that it affects the osmotic pressures of the several constituents in a given solution to quite a different extent. The influence which hydration has on the ions is less than its influence on the undissociated molecules. Thus in the case of the most highly hydrated salt lithium chloride and the slightly hydrated salt cesium nitrate at $0.3 N$, the difference between the values of $d\pi/dC$ is 16% for the ions and 38% for the undissociated molecules. It is thus evident that hydration has some effect besides that due to the removal of "free" water.

4. Application to Chemical Equilibrium.

The law of mass action, the Nernst equation for the electromotive force of concentration cells, and the laws of the constancy of the solubility product and of constant concentration of the undissociated molecules are derived by combining certain thermodynamic equations with

¹ Equation 13a expresses the results for potassium chloride up to $0.5 N$.

van't Hoff's law. Above, it was shown that another empirical relation of the form,

$$d\pi/dC = RT(1 + kC^m), \quad (15)$$

more exactly expresses the relation between osmotic pressure and concentration for the various molecular species present in a dilute solution of a di-ionic electrolyte. Although this is probably as convenient an equation as any that can accurately express the results, it is not thought that any particular theoretical significance can be attached to its form.

The combination of one such equation for the ions and of one for the undissociated molecules with the thermodynamic equation (1) yields an integrated equation containing five constants. Such an equation could almost certainly be made to agree with conductance data, though the calculation of the constants would be rather laborious. Since the fundamental equation (15) is more efficiently tested by means of conductance and freezing-point data combined by the method of the preceding sections, the five constant equations will not be applied to conductance data alone.

The application of equations similar to (15) to the data regarding the effect of the presence of one salt upon the solubility of another is of interest, since it should give evidence concerning the influence of one constituent of a solution upon the osmotic pressure of another. The full discussion of this subject is a lengthy matter and will not be entered upon here.

By combining an equation for the ions of the form (15) with the thermodynamic equation (10) and integrating, the relation¹

$$E = 2N_eRT/F [\ln C_1/C_2 + k/m (C_1^m - C_2^m)] \quad (16)$$

is obtained for the electromotive force of a concentration cell. This relation reduces to the Nernst equation when $k = 0$.

For potassium chloride solutions, with electrodes reversible to the anion at 13°, the numerical equation obtained from (13) is

$$E = 0.05634 \log C_1/C_2 - 0.00653 (C_1^{0.207} - C_2^{0.207}). \quad (17)$$

In Table IV values of E observed by Jahn² are compared with those calculated from the Nernst equation and those determined by means of Equation 17. Those calculated by the latter method agree with the data much better than do those deduced from the Nernst equation. The agreement of Equation 17 with the data is of course not proof independent of that drawn from freezing-point data that Equation 13 expresses the behavior of the ions of potassium chloride. It shows that the freezing-point data and the electromotive force measurements are consistent with each other.

¹ Here C_1 and C_2 are the ion concentrations of the two solutions.

² *Z. physik. Chem.*, 50, 162 (1904).

TABLE IV.—ELECTROMOTIVE FORCE OF CONCENTRATION CELLS OF POTASSIUM CHLORIDE.

| Concentrations. | | E. M. F. calculated. | | | |
|-----------------|----------|----------------------|------------------|------------------------|-------------------------------------|
| | | E. M. F. observed. | Nernst equation. | Percentage difference. | Equation 17. Percentage difference. |
| 0.04985 | 0.01969 | 0.02106 | 0.02183 | +3.6 | 0.02125 +0.9 |
| 0.03995 | 0.01969 | 0.01644 | 0.01664 | +1.2 | 0.01621 -1.4 |
| 0.03000 | 0.009924 | 0.02546 | 0.02620 | +2.9 | 0.02558 +0.5 |
| 0.01992 | 0.009924 | 0.01614 | 0.01654 | +2.5 | 0.01617 +0.2 |

5. Calculation of the Degree of Ionization.

The above calculations show in a quantitative manner the deviations from van't Hoff's law which the ions and the undissociated molecules exhibit if it be assumed that the degree of ionization is given by the conductance ratio. Jahn,¹ and recently Lewis,² have considered it to be more reasonable to assume that the concentration of the ions is proportional to their osmotic pressure or activity, than that it is proportional to the electrical conductance of the solution. Thus the latter calculated the degree of ionization at moderate concentrations, such as 0.1 *N*, upon the assumption that the concentration-activity ratio has at 0.1 *N* the same value that it has in more dilute solutions, such as 0.02 *N*. For this latter solution the degree of ionization was calculated from conductance data.

Parallel to the assumption that the ions are normal is the one that the undissociated molecules are normal. The degree of ionization may be calculated from freezing-point data upon either of these bases. This may be conveniently done by the following method. By combining the equation $\pi_i = RTC_i = RTC\gamma$, which represents the first assumption, with Equation 6 the following relations are obtained:

$$2RT(\gamma dC + Cd\gamma) = \gamma d\pi,$$

whence

$$1 + \frac{d \log \gamma}{d \log C} = \frac{d\pi}{dC} \div 2RT \quad (18)$$

The corresponding relation for the calculation upon the assumption that the undissociated molecules are normal is

$$1 + \frac{d \log (1 - \gamma)}{d \log C} = \frac{d\pi}{dC} \div RT. \quad (19)$$

Values for $d\pi/dC$ may be readily determined from freezing-point data by employing an equation similar to (7a), the differential ratio $\frac{d(\pi/C)}{d \log C}$ here also being determined by a graphic method. In this way $\frac{d \log \gamma}{d \log C}$ and $\frac{d \log (1 - \gamma)}{d \log C}$ may be computed for a series of concentrations.

¹ *Z. physik. Chem.*, 33, 545 (1900).

² *THIS JOURNAL*, 34, 1631 (1912).

If the value of the degree of ionization is known for one concentration, that for others may be accurately calculated. In order to obtain this value for one concentration, it may be assumed with Lewis that for the most dilute solution the conductance ratio gives the degree of ionization. It is better, however, if the data be sufficiently accurate, to determine this by a process of trial from the following considerations. The osmotic pressure of the undissociated molecules (or of the ions, if the assumption is that the molecules are normal) may be calculated in two ways: (1) by subtracting that of the ions calculated from the relation $\pi_i = RTC_i$, from the total osmotic pressure, (2) by calculating n by the method previously given,¹ then π_u/C_u by the aid of Equation 6 and finally the osmotic pressure of the undissociated molecules. Different values are chosen for the degree of ionization at the lowest concentration, until these two methods give agreeing results.

Values for the degree of ionization and for $d\pi_u/dC_u \div RT$, for solutions of potassium chloride, calculated upon the assumption that the ions are normal, are given in Table V. The probable error of the degree of ionization, and above 0.02 *N*, of that of the differential ratio, is about 1%. The results show that the deviation of the undissociated molecules from van't Hoff's law is practically as great in the very dilute solutions and greater above 0.005 *N* in this case than it is when the degree of ionization is calculated from conductance data.

TABLE V.—CALCULATION OF THE DEGREE OF IONIZATION ASSUMING THAT (A) THE IONS ARE NORMAL, (B) THE UNDISSOCIATED MOLECULES ARE NORMAL.

| Equivalents per liter. | (A) Assuming $\pi_i = RTC_i$. | | (B) Assuming $\pi_u = RTC_u$. | |
|---------------------------|--------------------------------|----------------------|--------------------------------|----------------------|
| | 100 γ . | $d\pi_u/dC_u + RT$. | 100 γ . | $d\pi_i/dC_i + RT$. |
| 0.001 | 97.00 | 1.14 | 99.50 | 0.978 |
| 0.002 | 95.30 | 1.224 | 99.04 | 0.981 |
| 0.005 | 92.42 | 1.310 | 97.73 | 0.985 |
| 0.01 | 89.78 | 1.353 | 95.72 | 0.995 |
| 0.02 | 86.61 | 1.384 | 92.02 | 1.024 |
| 0.05 | 81.63 | 1.410 | 82.3 | 1.16 |
| 0.1 | 77.43 | 1.423 | 68.2 | 1.50 |
| 0.2 | 72.7 | 1.43 | 43.9 | 3.+ |

Table V also gives the results of calculating the degree of ionization upon the assumption that the undissociated molecules are normal. In this case the degree of ionization for the very dilute solutions is greater than that calculated from conductance data, while at higher concentrations it is much less. In this case the uncertainty of the degree of ionization at 0.001 *N* is about 0.2%. Although at low concentrations the ions are practically normal, at higher concentrations their osmotic pressure is very much greater than that calculated from van't Hoff's law.

¹ THIS JOURNAL, 35, 524 (1913).

There are then, among others, the following three assumptions which may be employed for the calculation of the degree of ionization of solutions of strong electrolytes:

- (1) The degree of ionization is given by the conductance viscosity ratio.
- (2) Van't Hoff's law is obeyed by the ions.
- (3) Van't Hoff's law is obeyed by the undissociated molecules.

Experimental data show that in general only one of these assumptions can be true in the case of strong electrolytes. The acceptance of any one compels the rejection of the other two.

In view of the fact that many text-books and journal articles still present a misleading discussion of the calculation of the degree of ionization from freezing-point data, and since this calculation assumes that assumptions (2) and (3) are both true, it seems desirable to show in another way that the acceptance of one necessarily leads to the rejection of the other.¹ The differentiation of the mass law relation $C_i^2/C_u = K$ and the elimination of K from this equation and the derived differential equation gives

$$2dC_i/C_i - dC_u/C_u = 0.$$

This relation must hold if the mass law is obeyed. By eliminating C_i and C_u from this equation and from the thermodynamic equation,

$$2d\pi_i/C_i - d\pi_u/C_u = 0, \quad (1)$$

it is seen that the necessary and sufficient condition that the law of mass action hold over a certain concentration range is that at all concentrations

$$d\pi_i/dC_i = d\pi_u/dC_u.$$

The computation of the mol-number i from freezing-point data, and the calculation of the degree of ionization on this basis, assumes that both the ions and the undissociated molecules are normal. That is, it assumes

$$d\pi_i/dC_i = d\pi_u/dC_u = RT,$$

which is equivalent to assuming that the law of mass action holds. The results derived from such calculations do not obey this law and hence the method is inconsistent and theoretically incorrect. That the degree of ionization calculated by this method, in some cases, shows good agreement with that calculated from conductance data, is due to the fact that the deviation of the ions in one direction practically balances that of the undissociated molecules in the other, as far as the total osmotic pressure is concerned. It has long been recognized that actual gases are not "perfect" gases. Unfortunately the idea that, in general, solutes may be treated as normal or "perfect" solutes is much more persistent.

The probability of the validity of each of the above three assumptions will now be briefly considered.

¹ For a somewhat similar discussion see Washburn, *THIS JOURNAL*, 32, 484 (1910).

The Conductance Method.—Kohlrausch's principle of the independent migration of ions affords a theoretical basis for the first assumption. It gives an idea of the mechanism of electrical conduction in solutions and of the factors upon which it depends, *viz.*, the number of carriers, the charge upon each and their mobility in the given solution.

The determination of transference numbers supports the conductivity method of calculating the degree of ionization. It shows that at least up to about 0.1 *N* there is no certain change in the relative mobilities of the ions. These values may not be determined by the ordinary gravimetric method or by the less accurate moving boundary method. These give the Hittorf or ordinary transference numbers, whose value is affected by the amount of water carried by the ions as water of hydration. The true transference number must be determined by the aid of a reference substance. These values change much less with the concentration than do the Hittorf numbers.

It is probable that in concentrated solution the true transference number of many salts is not the same as it is in dilute solution. Two causes operate to bring this about: (1) the relative sizes of the ions change, due to a change in the degree of hydration with the concentration; (2) the change of the viscosity of the solution may affect the two ions unequally. Thus lithium chloride, which of the common uni-univalent salts shows the greatest change in its true transference number, is also the most highly hydrated and its solutions show the greatest relative viscosity. Even in the case of the much discussed hydrogen ion the best evidence indicates that its mobility is constant.¹ There appears then, to be no reason—except possibly that van't Hoff's law is not obeyed—for doubting that in principle the assumption of Kohlrausch is correct and that up to 0.1 *N* the degree of ionization may be calculated within a few tenths of one per cent. from the conductance data.

The Osmotic Pressure or Activity Methods.—Against the method of calculating the degree of ionization upon one or other of the assumptions that the ions or the undissociated molecules are normal may be urged, in the first place, the objection that the acceptance of one of these assumptions necessitates the rejection of the other. The choice between them is difficult to make. There is no more reason, either theoretical or experimental, for choosing one proposition than there is for choosing the other. They are exactly similar and apparently equally probable.

In the second place, there are a number of considerations which show that van't Hoff's law cannot be of general application. For this law to hold at different temperatures it is necessary that the heat of dilution (*q*) of the solution be zero. This quantity is usually small, but in general has an appreciable value. Even that part of the law corresponding to

¹ Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

Boyle's law ($\pi = kC$) cannot in general be true for solutions. This would hold only in the case that at all concentrations the percentage change with the concentration of q and of π were the same. This is seldom, if ever, the case.

None of the more common relations between the colligative properties and concentration can hold for the solutions which are formed when two immiscible liquid phases are in equilibrium. For, if the laws of Raoult or of van't Hoff held, the concentration of each constituent would be the same in the two phases, that is, the phases would be identical.¹

Thirdly, there is no theoretical relation between any one of the colligative properties and concentration.² Thus the van't Hoff law, particularly for solutions of electrolytes, apparently cannot be derived from better established, more fundamental or simpler, assumptions. Although a number of derivations for this law have been given, some of them even claiming to be thermodynamic in character, all involve assumptions which are *a priori* no more probable than is van't Hoff's law. Thus many of them rest upon the assumption that corresponding to its concentration in the solution and directly proportional to it, each molecular species has a definite concentration in the vapor phase (Henry's law) and that in this phase each constituent obeys Boyle's law. Thus above a solution of potassium chloride, there would be, in the gaseous phase, potassium chloride molecules and potassium and chloride ions (hydrated of course) proportional in concentration to the concentration of the same species in the solution and obeying Boyle's law.³

If a satisfactory explanation of the mechanism of osmotic pressure could be suggested, corresponding to that generally accepted as the mechanism of electrical conduction, it would aid materially in discussing the relation between osmotic pressure and concentration. The similarity in form between van't Hoff's law and the gas laws is no argument in favor of the former; osmotic pressure is not due to the unordered heat motions of the molecules of the solute; its origin is not similar to that of the pressure in the case of a gas.⁴

It is an empirically established fact that in the case of many dilute solutions of nonelectrolytes, the osmotic pressure is practically propor-

¹ Washburn, *Trans. Am. Electrochem. Soc.*, **22**, 330 (1912).

² Rosanoff and Dunphy (*THIS JOURNAL*, **36**, 1411 (1914)) claim to have shown that for an infinitely dilute solution Raoult's law follows from the Duhem-Margules equation. In their argument they confuse finite quantities and differentials; their proof involves the equating of infinitesimal quantities to unity!

³ The laws of thermodynamics which appear to some to demand the existence of such species in the vapor phase, must be applied with great caution to such phenomena, because these laws can be applied to molecular phenomena only when a relatively large number of molecules are involved.

⁴ Findlay, "Osmotic Pressure," p. 69, Longmans, Green & Co. (1913); Washburn, "Principles of Physical Chemistry," p. 161, McGraw-Hill (1914).

tional to the concentration. In general, the more nearly the solute and solvent resemble one another, the more nearly is van't Hoff's law obeyed. The expectation that the ions and the undissociated molecules of strong electrolytes should obey this law is based entirely upon analogy. This analogy cannot hold for both molecular species; it must break down in one case or in the other, or in both. There is, apart from conductance data, apparently no means of telling which of these alternatives to choose. It seems, then, reasonable to accept fully the evidence afforded by such data, to the effect that neither the ions nor the undissociated molecules are normal, and to calculate the degree of ionization from conductance measurements.

6. The Deviation from the Law of Mass Action.

It was shown above that the necessary and sufficient condition that the law of mass action hold over a given concentration range is that $d\pi_i/dC_i = d\pi_u/dC_u$ at each concentration. This condition is fulfilled when both molecular species obey van't Hoff's law. Calculations show that under none of the three assumptions used for calculating the degree of ionization (see page 1439) does the above relation hold. This is simply another way of stating the fact that the law of mass action does not hold in solutions of strong electrolytes. This fact has been considered by some to constitute a serious objection against the theory of electrolytic dissociation. The validity of the well-known expression for equilibrium in solutions of electrolytes is, however, no more a necessary consequence of this theory than is van't Hoff's law. The arguments against the theory based on the deviation of the strong electrolyte from the mass law have been, to a great extent, founded upon a misunderstanding of the basis for that law and have been given much more weight than their importance justifies.

It is apparently fairly generally held that even though the mass law is not obeyed at ordinary concentrations, it must, for thermodynamic reasons, hold for the infinitely dilute solution. Even in this case there is no theoretical reason why $d\pi_i/dC_i$ should equal $d\pi_u/dC_u$. The calculations which have preceded show that these ratios at ordinary concentrations may be expressed by equations, which, when extrapolated to infinite dilution, do give the same value (RT) for both. This empirical fact probably affords the best basis for the belief that at infinite dilution the law of mass action is obeyed by solutions of strong electrolytes.

It should be noticed that the magnitude of the deviation of the strong electrolyte from the normal behavior depends greatly upon the way in which this deviation is expressed. The equilibrium expression C_i^2/C_u increases with the concentration. Thus for potassium chloride it increases from 0.026 at 0.0001 N to 0.55 at 0.1 N , an increase of 2100%. Table I shows that this behavior, when expressed in terms of a deviation from van't Hoff's law, is accounted for by a deviation at 0.1 N of 3.3% for the

ions and of 37% for the undissociated molecules. The percentage deviation, when expressed in terms of osmotic pressure, is smaller than when expressed, as Lewis¹ has done, in terms of activity; this follows from the logarithmic relation between the two.

The fact that the ratio $\frac{d\pi_i}{dC_i} / \frac{d\pi_u}{dC_u}$ is, for many salts, nearly constant over a considerable concentration range is connected with the fairly general application of Storch's equation. This ratio, as is seen from Equation 9, is equal to $n/2$, n being the exponent in Storch's equation. The quantity $2-n$ is evidently another measure of the deviation of strong electrolytes from the law of mass action.

Arrhenius² has discussed this deviation in terms of the dissociating power of the solution and has explained it as being due at least in part to neutral salt action. Walden³ has been somewhat more specific and ascribes the change of dissociating power to a change in dielectric constant of the solution with change in concentration. It makes but little difference which we refer to as the cause of the deviation from the mass law, the change in dissociating power, or the departure from van't Hoff's law. There cannot be a change in dissociating power so defined, without a deviating from van't Hoff's law and *vice versa*.

Each method of discussing the behavior of the strong electrolyte offers its own advantages. The discussion in terms of osmotic pressure and concentration is valuable because it employs easily definable and readily measured quantities, but particularly because it differentiates between the behavior of the ions and that of the undissociated molecules, and shows the extent to which each is responsible for the deviation from the various simple equilibrium relations.

7. Summary.

1. Methods are developed and applied, by means of which the osmotic pressure of the ions and of the undissociated molecules at various concentrations are calculated for solutions of electrolytes. Conductance data, together with measurements of one of the colligative properties of the solution are employed for the calculation.

2. The assumptions involved in these calculations, besides the laws of thermodynamics, are that (a) in a solution of a di-ionic electrolyte the two ions behave similarly as regards their osmotic pressure-concentration relations, and that (b) the degree of ionization (γ) may be calculated from conductance and viscosity data, the concentration of the ions and of the undissociated molecules being $C\gamma$ and $C(1 - \gamma)$, respectively.

¹ THIS JOURNAL, 34, 1631 (1912).

² "Theories of Solution," p. 172, Yale University Press (1912); J. Chem. Soc., 105, 1414 (1913).

³ THIS JOURNAL, 35, 1649 (1913).

3. The differential ratio $d\pi/dC$ gives more exact information regarding the properties of the solution at any given concentration than does the direct relation π/C between osmotic pressure and concentration, and for many purposes is more important.

4. The uncertainties in the values for the ions and for the undissociated molecules, due to errors in the freezing-point and conductance data and in the value chosen for the equivalent conductance at zero concentration, are discussed.

5. The osmotic pressure of the univalent ion is in general a few per cent. less than that calculated from van't Hoff's law. That of the undissociated molecules of strong uni-univalent electrolytes is considerably greater; even at $0.0001 N$ the deviation is about 15%.

6. The bivalent ions deviate much more from van't Hoff's law than do the univalent ions. On the other hand, the undissociated molecules of bi-bivalent salts rather closely obey that law; their deviation is practically constant between $0.001 N$ and $0.02 N$.

7. At concentrations up to about $0.05 N$ the various univalent ions behave practically the same as regards their osmotic pressure-concentration relation. The same applies to the bivalent ions. Thus assumption (a) of paragraph 2 above, is supported.

8. The relation between osmotic pressure and concentration for both univalent and bivalent ions may be expressed, within the experimental error of the freezing-point determination, by an equation of the form $d\pi_i/dC_i = RT(1 + kC_i^m)$. In dilute solution a similar relation expresses the behavior of the undissociated molecules. In the case of potassium chloride the agreement is such that between $0.001 N$ and $0.5 N$ the total osmotic pressure calculated from such relations agrees with the experimental values with an average deviation of but 0.10%.

9. Hydration increases the osmotic pressure of both molecular species in the solution but influences that of the undissociated molecules to a greater extent than it does that of the ions. It hence has some effect other than the removal of "free" water from the solution.

10. Applications of the empirical relation between osmotic pressure and concentration to various equilibria are pointed out. That to electromotive force phenomena is illustrated.

11. The validity of the assumption used in the above calculations that (a) the degree of ionization is given by the conductance-viscosity ratio is discussed. The results to which this leads are compared with those which follow when the degree of ionization is calculated from freezing-point data upon either of the assumptions that (b) the ions are normal, or that (c) the undissociated molecules are normal. From the nature of the experimental data it follows that only one of these three assumptions can be true.

12. It is shown that assumption (a) has better theoretical and experimental support than have either of the other two assumptions.

13. The calculation of the degree of ionization from freezing-point data by the aid of the mol-number i assumes that assumptions (b) and (c) of paragraph 11 both hold and hence is theoretically incorrect.

14. It follows from the thermodynamic expression for equilibrium in solutions of electrolytes, that the necessary and sufficient condition that the law of mass action hold over a given concentration range is that $d\pi_i/dC_i = d\pi_u/dC_u$ for all solutions within this range.

15. There is nothing in the simple form of the electrolytic dissociation theory which necessitates the conclusion that the ions and the undissociated molecules of electrolytes obey van't Hoff's law. If they do not obey this law, the law of mass action cannot be followed. Hence the fact that solutions of strong electrolytes deviate from the requirements of the mass law is no argument against the theory of electrolytic dissociation.

16. The deviations from the law of mass action may be conveniently discussed in terms of the deviation of the ions and of the undissociated molecules from van't Hoff's law.

PASADENA, CAL.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF ILLINOIS. PUBLICATION No. 22.]

POTASSIUM CHLORIDE CONCENTRATION CELLS.

BY DUNCAN A. MACINNES AND KARR PARKER.

Received March 27, 1915.

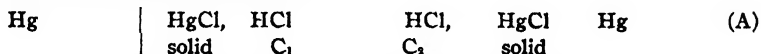
1. Purpose and Outline of the Investigation.

As a method for studying salt solutions, the determination of the electromotive force of concentration cells has the advantage, when compared with the freezing-point measurements, that the temperature at which the determination is carried out is not fixed, and may be kept constant at any desired point. This advantage is shared by vapor-pressure lowering and osmotic-pressure measurements, but the experimental difficulties have been found to be great in these determinations, particularly so when dilute solutions are investigated. It is, therefore, rather surprising that this method of attack of problems connected with salt solutions has not received more attention, since the thermodynamic relations connecting the results of the measurements of the electromotive force of concentration cells with the colligative properties of the solutions may readily be derived. The presence of liquid junctions in most concentration cells, and the uncertainty as to the method of correcting for them, may have contributed to the comparative neglect of this field. The present investigation was undertaken with the double purpose of measuring the free energy of dilution of potassium chloride by the electromotive

force method, and of investigating liquid junctions connecting salt solutions of different concentrations, by comparing the electromotive forces of cells in which these junctions are present with similar measurements on cells constructed so as not to involve this somewhat troublesome point of contact.

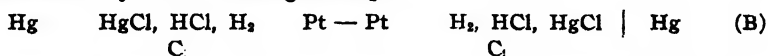
Among the few investigations yielding results suitable for interpretation in connection with the study of strong binary electrolytes is the accurate and much-discussed work of Jahn¹ on concentration cells of very dilute solutions of potassium and sodium chlorides and hydrochloric acid. Determinations of the electromotive force of concentration cells of hydrochloric acid have been made by Tolman and Ferguson.² Bell and Feild³ and Cumming⁴ have investigated cells containing silver nitrate solutions. There are, of course, many other measurements of the electromotive force of concentration cells in the chemical literature, but they deal with a single pair of solutions, are of doubtful accuracy, or else the solutions involved contain polyvalent ions. The latter introduce complexities which it is out of the province of the present paper to discuss.

Two forms of concentration cells have been investigated. The first, of which the following is typical:⁵



consists of two nonpolarizable electrodes in equilibrium with solutions, of concentrations C_1 and C_2 , which are connected by a liquid junction. Cells of this type were employed in Jahn's researches, and are usually called "concentration cells with transference."

The second variety, "concentration cells without transference," may be represented by the following example:



These are composed of two independent cells, and involve no liquid junction. This latter type has been the subject of a research by Tolman and Ferguson.⁶

The cells without diffusion are capable of simpler theoretical interpretation, as will be shown in the next section. There is, however, the experimental difficulty of finding a reversible electrode for *both* the ions of

¹ *Z. physik. Chem.*, **33**, 545 (1900).

² *THIS JOURNAL*, **34**, 232 (1912).

³ *Ibid.*, **35**, 715 (1913).

⁴ *Trans. Faraday Soc.*, **2**, 213 (1907).

⁵ In this paper the conventions adopted in the bibliography by Abegg, Auerbach and Luther, "Messungen electromotorischer Kräfte galvanischer Ketten" will be followed. A vertical line represents a junction; solid-liquid or liquid-liquid. A positive value for the E. M. F. means that current tends to flow from right to left through the cell.

⁶ *Loc. cit.*

ion in the direction of the current (from G' to G) and the migration of $(1 - \eta_K)$ equivalents of chloride ion in the reverse direction, where η_K is the Hittorf transference number of the cation. Thus the total effect of the operation of the cell will be the transfer of η_K equivalents of potassium chloride from the solution of the concentration $C + dC$ to one of

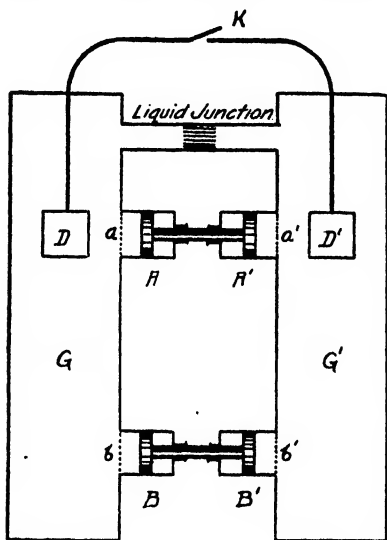


Fig. 1.

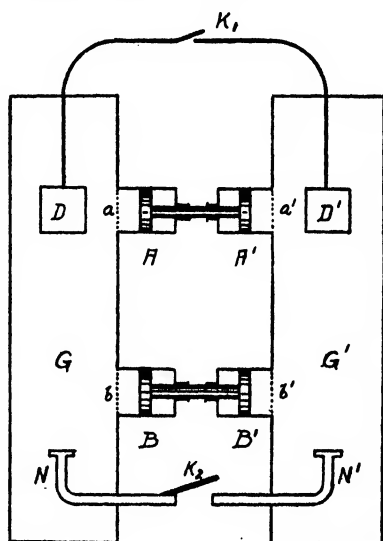


Fig. 2.

the concentration C . To compensate for this change and to maintain a constant difference of concentration the pistons $A - A'$ and $B - B'$ are moved reversibly toward the right, withdrawing η_K mols of each ion from chamber G and forcing them into chamber G' . As the electrical energy must be equal to the osmotic work, the following relation holds:

$$FdE = \eta_K (V_{K^+} d\Pi_{K^+} + V_{Cl^-} d\Pi_{Cl^-}) \quad (1)$$

in which E is the electromotive force and V_{K^+} and V_{Cl^-} are the volumes of solution containing one gram equivalent of ion.

Fig. 2 is a thermodynamic engine for the cells without transference. It is similar to that shown in Fig. 1 except that the liquid junction has been replaced by the electrodes $N - N'$, which, in the case under discussion, are potassium amalgam electrodes. The concentrations of the salt are C and $C + dC$ in the chambers G and G' as before. On closing keys K_1 and K_2 and allowing F coulombs to pass, one gram equivalent each of potassium ion and of chloride ion will be formed in chamber G and a like amount will be removed by the electrodes from chamber G' . To maintain equilibrium the pistons $A - A'$ and $B - B'$ must be moved reversibly toward the right, each through a volume containing one gram

of silver chloride, of a reddish brown color, the shade of which was the same whether the electrolysis was carried out in the light or in complete darkness.

Forty electrodes were made in this manner in sets of eight. Electrodes chosen at random from different sets were checked against each other

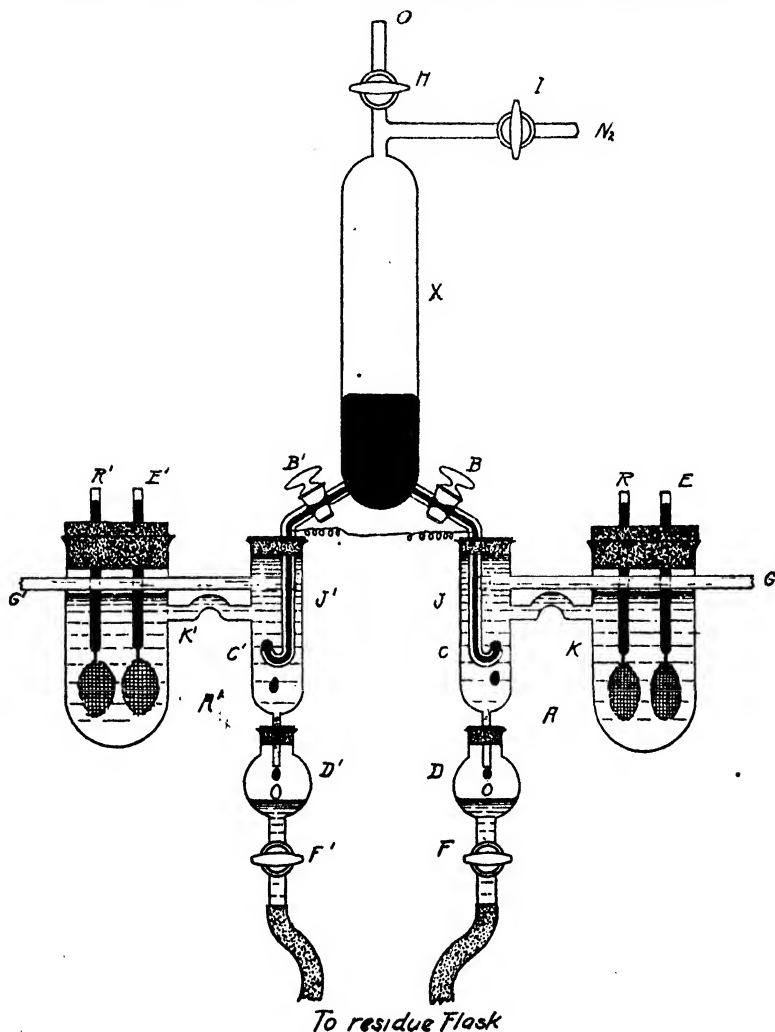


Fig. 3.

frequently, with the result that "normal"¹ electrodes were always found to be within a few tenths of a millivolt of each other. When polarized

¹ Two kinds of abnormal electrodes were encountered (a) those which became abnormal because of the attack of a parasitic mold, and (b) those in which a white

by the application of one millivolt they returned to their original potential in a few minutes. New electrodes from one set generally showed potential differences of only a few hundredths of a millivolt. There was a slight ageing effect noticed, the older electrodes being electropositive to the newer ones. As this effect was always in the same direction and of the same magnitude within 0.05 mv. no error arose from this source, since similar electrodes were always opposed to each other.

(b) **The alkali metal amalgam electrode** employed is represented by *X* in Fig. 3. It differs from that used by Lewis and his associates only in having two capillary outlets *J* and *J'* for the amalgam, in order that it could be used in the two half cells at one time. To fill the electrode cell with the amalgam, the amalgam reservoir shown in Fig. 4 was inverted and connected by a T-tube to *O* in Fig. 3. The other branch of the T-tube was then connected to the Gaede pump. After exhausting and thoroughly drying the cell, the stopcock to the amalgam reservoir was opened and the amalgam was run from the reservoir. Dry, pure nitrogen was then introduced through the tube marked *N*₂. The surface of the amalgam either remained bright after the introduction of the nitrogen or else an exceedingly thin film slowly formed over the surface.

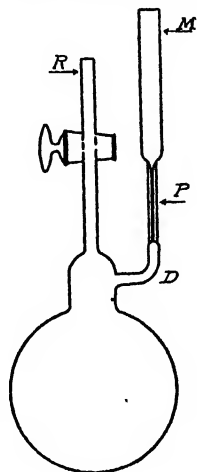


Fig. 4.

The potassium amalgam was prepared by a method which is a simplification of that used by Lewis and Kraus.¹ A diagram of the vessel used for this purpose is shown in Fig. 4. It consists of a distilling flask with allotropic silver chloride appeared to be formed in place of the "normal" plum colored AgCl.

(a) Some of the electrodes were attacked by an organism after some weeks, although the solutions in which they were placed were made up from conductivity water and pure KCl. The electrodes so attacked invariably became electrically different from the "normal" ones, developing in some cases a potential difference as high as 10 mv. This potential difference was always in the same direction, negative to the "normal" electrode. The mold was investigated by Dr. F. L. Stevens of the Botanical Department of the University of Illinois and, although conditions were very unfavorable for its development and culture, was identified as a parasitic mold (*Aspergillus*).

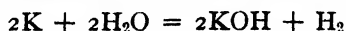
(b) The second class of "abnormal" electrodes appeared to have an allotropic form of AgCl on their surface. This form of AgCl, white in color and unaffected by diffused daylight even after weeks of exposure, sometimes appeared in spots on a "normal" electrode and sometimes covered the entire surface. These electrodes were always electronegative to the "normal" electrodes by varying amounts. The electrodes were all prepared under like conditions and the reason for the development of this modification of AgCl on some electrodes and on certain spots on a "normal" electrode is not clear.

¹ THIS JOURNAL, 32, 1459 (1910).

a stopcock fitted to its neck and a capillary tube, P , of about 0.4 mm. bore, sealed at one end to the delivery tube of the flask and at the other end to the tube M with an internal diameter of 6 mm. Pure mercury was first poured into the carefully dried apparatus. Pellets of potassium were placed in the tube M , which was then fused together at upper end. These pellets can be conveniently made by forcing a cork borer into a piece of the metal and then pushing the resulting small cylinder of the metal directly into the tube M by means of a closely fitting glass tube. The surface of the metal thus obtained was covered with a very thin film of oxide. The whole apparatus was next evacuated through the tube R by means of a Gaede pump. The pumping was continued for half an hour or more, during which time the apparatus was gently warmed to aid in removing the last traces of air and moisture from the mercury, after which the side tube from M to D was slowly and uniformly heated with a small, free flame. The potassium soon melted and passed through the capillary, collecting as a brilliant spot of metal in the bend of the tube at D . The capillary was then sealed off at P and the whole apparatus inverted, thus bringing the potassium and mercury into contact. The amalgamation took place quietly, little heat being evolved. When solution was completed, the apparatus was shaken for some time in order to be sure that the resulting amalgam was uniform. In appearance the surface to the amalgam was as bright as the mercury from which it was prepared. Amalgams of various concentrations were prepared from the stock amalgam by diluting, *in vacuo*, with pure mercury.

4. Design and Operation of the Cell.

The apparatus for the concentration cell without transference is shown in Fig. 3. The design finally adopted is the result of considerable preliminary experimenting, as it was found that there were a number of obstacles in the way of realization of complete reversibility at the amalgam electrode. One of the greatest difficulties was the side reaction:



It thus takes place a rapid drop of the potential between the electrode and solution must follow, since the concentration of the amalgam is thereby lowered and the ion concentration in the immediate vicinity of the electrode is increased. This difficulty was, it is believed, entirely overcome by having a constantly moving amalgam. The arrangement of the cell also permits the immediate removal of the drops of amalgam as they get detached, since they fall directly into bulb D and thence into the residue flask. Streams of fresh solution, run in through the tubes G and G' , were made to pass by the amalgam electrodes. This made sure that measurements were carried out with solutions uncontaminated by the passage of the amalgam. The air spaces in the bulbs D and D' permitted

the worker to observe the rapidity of the flow of the solution and prevented short circuiting through the rejected material or through the thermostat water. It was found that readings of the voltage of this cell became constant within about 0.05 millivolt when the flow of amalgam was about thirty drops per minute. After this an increase in the rate of flow had no influence on the results. The rate of flow of the solution was also found to have no influence, above a certain minimum. It is apparent that the effect of the side reaction given above was eliminated by this arrangement and also that the amalgam had time to come to electrical equilibrium in the short time that it was in contact with the solution. The formation of hydrogen was never observed in the cell, even when very few drops of amalgam per minute were passing.

The separation of each half cell into two portions, C , K and C' , K' , made it possible to leave the Ag , AgCl electrodes in contact with solution with which they were in equilibrium and which was also not disturbed by the solution flowing past the amalgam electrodes. The bent connecting tube aided in preventing mixing.

Early in the investigation it was recognized that oxygen dissolved in the solutions can influence the results on account of the side reaction:



and for this reason the solutions were prepared so that they came in contact with the air for only a very short time. The effect of this side reaction is the same as the previous one, *i. e.*, to lower the electromotive force, since the addition of potassium ions to both solutions will lower the ratio of the ion concentrations.

The solutions were made at first by collecting the water very hot in "Resistenz-glas" bottles from the still used for preparing conductivity water, pumping out the air remaining above the water and replacing it by pure nitrogen. The correct amount of salt necessary to make a solution of the required strength (in mols per liter) with all weights calculated to vacuum standard, was then added in a small glass capsule and allowed to dissolve. A small amount of air was carried into the solution in this last operation. Table I gives measurements of the E. M. F. of the cell:

| | | | | |
|----|--------------------|-------------------------------------|----------------------|----|
| Ag | AgCl, KCl 0.5 N | KHg _x — KHg _x | KCl, AgCl 0.005 N | Ag |
|----|--------------------|-------------------------------------|----------------------|----|

the solutions in which were made as has just been described, using amalgams of widely varying concentration in the amalgam electrode.

TABLE I.

| Conc. of amalgam | 0.02% approx. | 0.002% approx. | 0.0002% approx. |
|------------------|--------------------|--------------------|------------------|
| E. M. F. | +0.10603 ± 0.00001 | +0.10600 ± 0.00001 | +0.1060 ± 0.0005 |

These figures indicate that the electromotive force is independent of the concentration of the amalgam within wide limits. The amalgam in

the last determination was too dilute to allow the most accurate measurements to be made. When, however, the results of several series of determinations similar to the above, and involving solutions of different concentrations, were plotted, irregularities appeared which could only be explained by assuming that the small amount of dissolved oxygen remaining in the solution reacted instantaneously with the amalgam, lowering the potential at both amalgam-solution boundaries. As can be seen from Table I this effect is, however, surprisingly constant. Accordingly, the final measurements were made using solutions from which every trace

of oxygen was excluded.

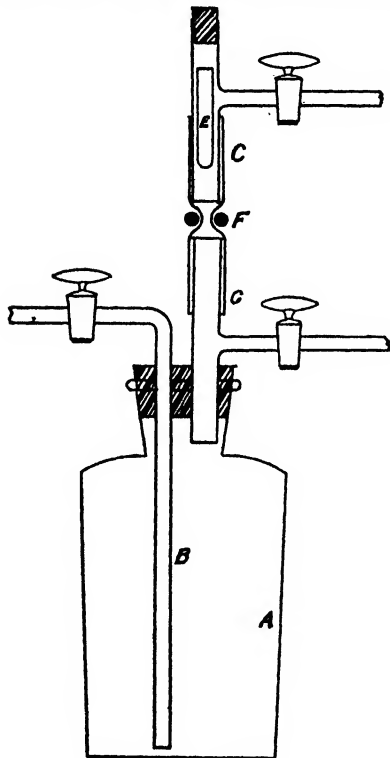


Fig. 5.

of oxygen was excluded. The apparatus used for preparing the air-free solutions is shown in Fig. 5. The stopper of the "Resistenz-glas" bottle *A* is fitted with two tubes. Tube *B*, which reaches to the bottom of the flask, is used for the delivery of the solution to tube *G* of Fig. 3. Tube *C*—*C'* is in two parts, which may be shut off from each other by a piece of carefully cleaned rubber tubing and a pinch-cock, represented by *F*. Both parts are fitted with stopcocks, as shown. In making the solution, the water was collected by placing the outlet from the still well within the mouth of the bottle and regulating the flow through the condenser of the still so that the water was collected as hot as possible and the air originally in the bottle was displaced by the large volume of steam which was evolved. When the bottle was nearly full, the stopper was inserted, the tube *B* filled with water, and the water boiled for fifteen or twenty minutes by evacuating through the outlet from tube *C*. After this pure nitrogen was run in through this tube and the water allowed to cool with a pressure of this gas upon it. The required amount of salt was then weighed out into the capsule *E* and placed above the pinchcock in the tube *C'*, which was then closed at its upper end. After the air had been removed from this space by evacuating and filling with nitrogen several times, the capsule was made to drop into the water by opening the pinchcock *F*. The water in tube *B* was then displaced by nitrogen and the bottle was shaken until the solution was uniform.

Table II gives a summary of the results obtained from cells in which the solutions used were prepared in the manner just described.

TABLE II.—THE ELECTROMOTIVE FORCE OF POTASSIUM CHLORIDE CONCENTRATION CELLS WITHOUT TRANSFERENCE AT 25°.

| Ag | AgCl, KCl soln. | K ₂ Hg—K ₂ Hg | KCl soln. AgCl | Ag, E. M. F. |
|----|-----------------|-------------------------------------|----------------|--------------|
| " | Solid 0.5 N | 0.02% | 0.05 N solid | " — 0.10735 |
| " | " 0.5 " | 0.002% | 0.05 " " | " — 0.10745 |
| " | " 0.1 " | 0.004% | 0.01 " " | " — 0.10885 |
| " | " 0.1 " | 0.002% | 0.01 " " | " — 0.10900 |
| " | " 0.05 " | 0.004% | 0.005 " " | " — 0.11085 |
| " | " 0.05 " | 0.002% | 0.005 " " | " — 0.11085 |

The amalgam concentrations are approximate.

The electromotive force measurements were carried out with a Leeds & Northrup potentiometer which had been calibrated by the Bureau of Standards. The Weston Standard cell used was compared several times during the investigation with a similar cell which had recently been calibrated by the same Bureau. The measurements were carried out in a thermostat kept constant within 0.01°. The thermometer used was also calibrated by the Bureau of Standards.

5. The Concentration Cells with Transference.

Cumming and Gilchrist¹ have described the best conditions for the formation of liquid junctions giving reproducible results. These are (a) the use of wide tubes in making the connections, (b) the formation of a new boundary shortly before the measurements are taken, (c) the mechanical mixing of the solutions at the boundary. The cell used for the purpose in this investigation is shown in Fig. 6.

The vessels *M* and *M'* contain the identical silver-silver chloride electrodes used with solutions of the corresponding concentrations in the cells without transference. The tubes *L* and *L'*, of about 5 mm. internal diameter, are brought together

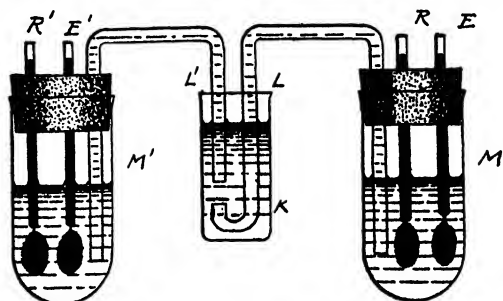


Fig. 6.

in the small vessel *K* which contains a solution formed by mixing together equal parts of the solutions contained in *M* and *M'*. The tubes can be readily filled by pressing the rubber stoppers deeper into the vessels *M* and *M'* or by placing a slight air pressure on the surface of the solutions by means of tubes (not shown) which pass through the stoppers. The "time change" which is apparently always present where a liquid

¹ *Trans. Farad. Soc.*, 9, 174 (1913).

junction is involved, was less than one millivolt per hour, and as new boundaries which gave the original reading could readily be obtained, it is believed that maximum values of the electromotive force were measured in each case.

The results of these measurements are given under Table III.

TABLE III.—ELECTROMOTIVE FORCE OF POTASSIUM CHLORIDE CONCENTRATION CELLS WITH TRANSFERENCE AT 25°.

| Ag | AgCl | KCl | | KCl | AgCl | Ag | E. M. F. |
|----|-------|------|---|-------|---------|----|----------|
| " | Solid | 0.5 | N | 0.05 | N Solid | " | —0.05357 |
| " | " | 0.5 | " | 0.05 | " | " | —0.05357 |
| " | " | 0.1 | " | 0.01 | " | " | —0.05400 |
| " | " | 0.05 | " | 0.005 | " | " | —0.05470 |
| " | " | 0.05 | " | 0.005 | " | " | —0.05475 |
| " | " | 0.01 | " | 0.001 | " | " | —0.0560 |

6. Purification of Materials.

Mercury.—The mercury used in this investigation was purified by passing it in a thin stream through a tube, a meter long, filled with dilute nitric acid, and then distilling with diminished pressure in a current of air.

Potassium Chloride.—A well known manufacturer's best grade of potassium chloride was recrystallized one or more times from conductivity water, and the mother liquor drained off with the help of a centrifuge. It was always fused immediately before using.

Nitrogen.—Since most of the operations carried out in this work were found to be disturbed by the presence of oxygen, even if present in very small amounts, a rather large volume of an inactive gas was found to be a necessity. Nitrogen was found to fill all the requirements. It was prepared from sodium nitrite and ammonium chloride as described by Tucker and Yang¹ and kept over water in a gasometer. To remove the small amount of oxygen remaining, as well as the moisture present, it was passed through a train consisting of sulfuric acid, soda lime, copper heated to redness, and when necessary, through U-tubes filled with P₂O₅. The copper, which had been reduced by hydrogen from copper oxide, was contained in a quartz tube. The latter was a convenience as it could be heated and cooled rapidly without danger of breaking.

7. Discussion of Results.

On page 1448 we obtained the differential equation

$$FdE = \eta(V_1 d\Pi_1 + V_2 d\Pi_2)$$

connecting the osmotic work and the electromotive force of a "concentration cell with transference," and the expression

$$FdE = V_1 d\Pi_1 + V_2 d\Pi_2$$

¹ Orig. Comm. 8th Int. Congr. Appl. Chem., 21, 121 (1912).

for a "concentration cell without transference." From these equations it is apparent that whatever the relations between II and V may be the ratio:

$$\frac{\text{E. M. F. of cell with transference}}{\text{E. M. F. of cell without transference}}$$

for cells containing the same pair of salt solutions, should be equal to the transference number of one of the ions. By referring to the derivation of the equations it can be seen that in the present case the ratio gives the transference number of the cation. The derivation, however, involves the assumption that thermodynamics can be applied to the cell containing the liquid junction. This, in the authors' minds, needed proof, since this point of contact of two solutions of different concentrations is certainly not in the ordinary sense of the word a system in equilibrium. Table IV gives values of the above ratio, and also, from Noyes and Falk's¹ most useful compilation, the values of the transference number obtained by the Hittorf and by the moving boundary methods.

TABLE IV.—COMPARISON OF THE TRANSFERENCE NUMBERS OF THE CATION IN KCl, AT 25°, OBTAINED BY THE E. M. F., HITTORF, AND MOVING BOUNDARY METHODS. .

| Concentrations. | E. M. F. ratio. | Transference numbers. | | |
|-----------------|-----------------|-----------------------|----------|----------------|
| | | E. M. F. | Hittorf. | Mov. boundary. |
| 0.5 — 0.05 | 53.57/107.4 | 0.498 | 496 | ... |
| 0.1 — 0.01 | 54.00/108.9 | 0.496 | 496 | 0.493 |
| 0.05 — 0.005 | 54.70/110.85 | 0.494 | 496 | 0.493 |

From these figures it is evident that the thermodynamic theory as outlined is confirmed within the experimental error. This method for the determination of the transference number was first suggested by Helmholtz.²

The general applicability of this method for obtaining transference numbers may be tested by comparing the value it gives of the transference number of the hydrogen ion in hydrochloric acid with that determined in the usual way. Jahn³ has found the E. M. F. of the following cells with transference at 18°:

| | | | | | | | | |
|----|---|-----------|------------|-----|------|---|----|--------------------|
| Ag | | AgCl, HCl | | HCl | AgCl | | Ag | E. M. F. |
| " | " | 0.03330 N | 0.003329 N | " | " | " | " | —0.09162 ± 0.00005 |
| " | " | 0.01665 N | 0.001665 N | " | " | " | " | —0.09235 ± 0.00005 |

and Tolman and Ferguson's⁴ paper contains measurements of the voltage of the cell without transference:

| | | | | | | | | | |
|----|---|-----------|--------|---------------------------------|---------|-----------|---|----|-----------------|
| Hg | | HgCl, HCl | | H ₂ — H ₂ | | HCl, HgCl | | Hg | E. M. F. |
| " | " | 0.02 N | 1 atm. | 1 atm. | 0.002 N | " | " | " | —0.1109 ± 0.001 |

at the same temperature. Making a linear interpolation from the elec-

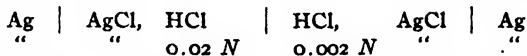
¹ THIS JOURNAL, 33, 1454 (1911).

² Ges. Abh., 1, 840; 2, 979.

³ Loc. cit., page 1446.

⁴ Ibid., page 1446.

tromotive forces of the first mentioned cells for a value of the voltage of the cell:



we obtain -0.09210 . The ratio $0.09210/0.1109$ is 0.830 , which agrees, well within the experimental error, with the directly determined transference number 0.833 , as given by Jahn¹ and by Drucker and Krsnjavi.²

On applying the integrated equations:

$$E = 2\eta RT/F \ln C'_i/C_i \quad (4)$$

$$E = 2RT/F \ln C'_i/C_i \quad (3)$$

for the electromotive force of a concentration cell with and without transference, respectively, to our data, and calculating ion concentrations in the usual way from conductance measurements, we do not find the same agreement of the theory with the results of experiment. It is found that in every case the calculated values of the electromotive force are too high. This is shown in a slightly different ways in Table V, in which the ratio of the ion concentrations C'_i/C_i obtained from the electromotive force measurements by means of Equation 3 are compared with the same ratios calculated from conductance data. Column I of the table gives the salt concentrations involved. Column II contains values of the ratio C'_i/C_i computed from the conductance measurements of Kohlrausch and Maltby³ at 18° . The measurements by Melcher⁴ on KCl solns. at 25° show that little error is involved in assuming that the ratio does change appreciably in the temperature range, 18° to 25° . The ratio as calculated from electromotive force measurements is placed in the last column. The values of R , T_0 , and F used in obtaining these last figures are $8,316$, 273.1 , and $96,500$, respectively, the last being the value of the Faraday recommended by Bates and Vinal⁵ for general use. It will be observed that the salt concentrations have the same ratio: 1 to 10, in each pair of solutions. The figures in italics refer to Jahn's work at 18° .

TABLE V.—RATIOS OF ION CONCENTRATIONS OF POTASSIUM CHLORIDE SOLUTIONS CORRESPONDING TO VARIOUS TEN TO ONE SALT CONCENTRATIONS.

| Salt concentrations. | C'_i/C_i from conductance measurements. | C'_i/C_i from E. M. F. measurements. |
|-------------------------|---|--|
| 0.5 -0.05 | 8.85 | 8.09 |
| 0.1 -0.01 | 9.16 | 8.33 |
| 0.05 -0.005 | 9.30 | 8.64 |
| <i>0.03349-0.003347</i> | 9.36 | <i>8.76</i> |
| <i>0.01669-0.001670</i> | 9.47 | <i>8.86</i> |
| 0.01 -0.001 | 9.62 | 9.04 |

¹ *Z. physik. Chem.*, **37**, 673 (1901).

² *Ibid.*, **62**, 731 (1908).

³ *Wiss. Abhandl. der Reichsanstalt*, **3**, 154 (1900).

⁴ *THIS JOURNAL*, **33**, 1669 (1901).

⁵ *Ibid.*, **36**, 916 (1914).

From these figures and from Fig. 7, where the ratios are plotted as ordinates, and the higher concentration of each pair of solutions as abscissae, it can be seen that, although the ratios differ widely when calculated by the two methods, both sets of figures are apparently approaching the same value: 10, which would be the ratio of the ion concentrations of two solutions both near infinite dilution, but whose total salt concentrations were in the proportion 10 to 1. In other words, the Nernst equation can be used to calculate the electromotive force of concentration cells of potassium chloride only when the solutions involved are near infinite dilution.

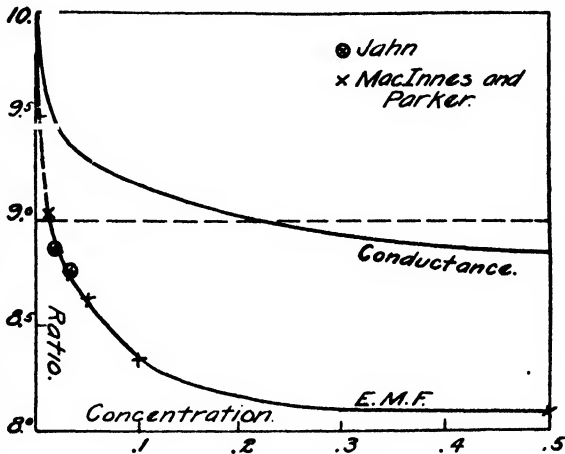


Fig. 7.

the electromotive force of concentration cells of potassium chloride only when the solutions involved are near infinite dilution.

Equations 3 and 4 may also be written

$$E = 2RT/F \ln a'/a$$

and

$$E = 2\eta RT/F \ln a'/a$$

where a and a' are the "activities"¹ of the ions. In this form the equations are, by definition, thermodynamically valid, provided the positive and negative ions in any solution have the same activity. The figures in the last column of Table V are therefore activity ratios. It is evident that the "activity" ratios approaches the "concentration" ratios as the solutions become more and more dilute.

In order to obtain an idea of the magnitude of the "activities" of the ions at various concentrations let us assume provisionally that at 0.001 N the activity of the ions is equal to their concentration as calculated by multiplying the total salt concentration by the conductivity ratio: Λ/Λ_0 . From this value, and the activity ratios given in Table V, we can calculate the activities corresponding to the salt concentrations 0.01 N and 0.1 N . The following table gives, for the concentrations mentioned, the values of the "activity" calculated as has been described, the usually accepted degrees of dissociation, and the "thermodynamically effective" degrees of dissociation which are obtained by dividing the activity by the corresponding total concentration.

¹ Lewis, *Proc. Am. Acad.*, 43, 259 (1907).

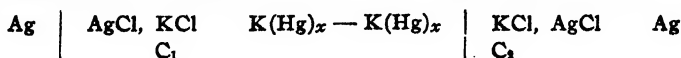
| Salt conc. | "Activity." | Degrees of dissociation. | "Thermodynamically effective" degrees of dissociation. |
|----------------|-------------|--------------------------|--|
| 0.001 <i>N</i> | 0.000979 | 97.9 | (97.9) |
| 0.01 <i>N</i> | 0.00885 | 94.1 | 88.5 |
| 0.1 <i>N</i> | 0.0738 | 86.1 | 73.8 |

Readers of Lewis' recent paper on "The Activity of Ions and the Degree of Dissociation of Strong Electrolytes,"¹ will recall that he decides from thermodynamic considerations on the basis of solubility and freezing-point measurements, that 74% is the effective or "corrected" degree of ionization of a 0.1 *N* solution of potassium chloride. The close agreement (0.2%) of this value with the one for the same concentration given in the table is not, as might appear at first sight, an independent piece of evidence in favor of this low degree of ionization, but simply means that measurements on all the colligative properties must lead to the same values of the activity of the ions if thermodynamic reasoning is employed.

That the conductivity method does not give the same degree of dissociation as the electromotive force or related methods has been known for some time, and has been explained in a number of ways. Jahn believed that the E. M. F. method gives the correct measure of ionization and accounted for the higher results from conductance data by assuming that the ions "speed up" as the concentration increases. Another explanation, which also starts from the lower values of the degree of ionization as the correct ones, makes use of the hypothesis that in addition to the usual conduction by ions the undissociated molecule also takes part in the conduction by a series of rapid dissociations and recombinations, usually known as the Grotthus chain effect. This would, obviously, increase as the salt concentration increases. Most of the investigators in this field, however, regard the conductivity ratio Δ/Δ_0 (or this ratio multiplied by some function of the viscosity) as the degree of dissociation, and consider the decreasing activity of the ions as the concentration increases as being due to a change of the nature of the solution as a solvent medium, due, in part at least, to the charges on the ions. Walden and others have shown that it is probable that the dielectric constant of water increases when electrolytes are added. It seems quite possible that neither degree of dissociation is the correct one and that all the influences mentioned may have their effect.

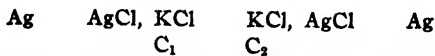
8. Summary.

The electromotive forces of the cells without transference:



have been measured and compared with measurements of the voltage of the cells with transference.

¹ THIS JOURNAL, 34, 1631 (1912).



With the same solutions in cells of both types, the ratio of the potentials is shown to give accurate values of the transference number of the cation.

The measurements indicate that the "activities" of the ions from potassium chloride are much lower than the concentrations as calculated from conductance measurements. The values of the "activity" and of the concentration, however, apparently approach the same limit for very dilute solutions.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, No. 250.]

THE DROP WEIGHT METHOD FOR THE DETERMINATION OF THE SURFACE TENSION OF A LIQUID.

By J. LIVINGSTON R. MORGAN.

Received April 12, 1915.

This method for the determination of the surface tension is one of the results of the extended, *purely experimental and statistical*, investigation of the relationship between the falling drop weight and the surface tension of a liquid, reports of which have appeared from time to time from this laboratory.¹ As no description of this method, in its present form, has appeared in any one place, however, for it has developed only gradually; and since some misunderstanding appears to exist concerning it; it is thought desirable that a brief résumé of the conditions necessary for its holding, in the light of the searching and conclusive, experimental tests to which it has been subjected in this laboratory, be presented here. This résumé will perhaps be of advantage also, in that it will render the future work published from this laboratory more intelligible; and, further, will make the method available to those other workers who may wish to determine accurate surface-tension values.

The drop weights considered throughout this work are those found by aid of the apparatus already described in some detail in *THIS JOURNAL*,² which enables one to determine with a high degree of precision the weight of any desired number of drops of liquid falling from any sharp-edged capillary dropping tip, at any fixed temperature below 90°; and that, *free from any effect of evaporation*, even when within but a few degrees of the boiling point of the liquid. The drops here are always formed very slowly, at any rate immediately before their fall, so that they drop unaided and of their own weight alone.

¹ See Morgan and co-workers, "The Weight of a Falling Drop and the Laws of Tate," in a series of eighteen papers, *THIS JOURNAL*, 30, 33 and 35 (1908-1913).

² Morgan, *THIS JOURNAL*, 33, 349-62 (1911).

As the result of an experimental study of some two hundred especially purified liquids and solutions, for more than one hundred of which the surface tensions (lying between 15.3 and higher than 76 dynes per centimeter), for purposes of comparison, are known from some other method; liquids which include those of every conceivable type, and possessing every property which could possibly and adversely influence the behavior; it has been found that *under certain definite conditions*, the drop weights of liquids from any one dropping tip are proportional to their surface tensions, at the same temperature.

Expressed mathematically, this relationship is

$$\frac{\gamma_{C_6H_6,t}}{w_{C_6H_6,t}} = \frac{\gamma_{H_2O,t'}}{w_{H_2O,t'}} = \frac{\gamma_{l,t''}}{w_{l,t''}} = \text{Constant}, \quad (1)$$

where, although the surface tension γ in the numerator of any one ratio must be at a temperature identical with that for the drop weight value w in its denominator, the γ values can be at any desired temperature, t, t' or t'' , and need not be even on the same portion of the scale.

Transforming this equation, we find

$$\gamma_{l,t''} = \left(\frac{\gamma_{C_6H_6,t}}{w_{C_6H_6,t}} \right) w_{l,t''} = \left(\frac{\gamma_{H_2O,t'}}{w_{H_2O,t'}} \right) w_{l,t''} = \text{Constant} \times w_{l,t''}; \quad (2)$$

the surface tension of any liquid at any temperature is equal to its falling drop weight from any one tip at that temperature, times a constant, the value of which is found once for all for that tip, and is equal to the ratio of the surface tension of some standard liquid to the drop weight of that liquid, both at some one, like, temperature.

This is one of Tate's laws which has been under *experimental* investigation in the series of papers alluded to above, and which has been *proven* to hold rigidly, under the definite conditions discussed below, for so many liquids. As is apparent, the method is a *relative*, not an absolute one, and consequently it must be standardized by aid of some selected liquid, preferably one which can be readily obtained in the pure state, and which has a comparatively high boiling point. Benzene and water have been employed in general for this purpose, for in addition to fulfilling the above requirements, they differ greatly as far as concerns the magnitude of the surface tension, and thus inspire increased confidence, perhaps, in the range of the method.

In order that the surface tensions of these liquids, for standardization purposes, may be readily calculated to the temperature at which their drop weights may have been found experimentally, use is made of the following interpolation formulas:

$$\gamma_{C_6H_6,t} = 30.514 - 0.1321t + 0.000082t^2,$$

$$\gamma_{H_2O,t} = 75.872 - 0.1547t - 0.00022t^2,$$

where γ is expressed in dynes per centimeter, and t may have any value up to 80° .

The above equation for benzene represents the average of *all* the results of *all* the accurate workers with benzene by the capillary rise method, and was obtained from them by aid of the method of least squares; it thus leads to the most accurate and representative average value of the surface tension of benzene at any temperature up to 80° .¹ The equation for water is that found by Morgan and McAfee² after standardizing their tip with benzene, and gives results which are in excellent agreement with the best results on water found by observers using other methods.

Conditions Necessary for the Holding of $\gamma_{t,t} = \text{Constant} \times w_{t,t}$.

The conditions necessary for the precise holding of the equation, $\gamma_{t,t} =$

¹ This equation, which is most convenient for laboratory purposes, gives results which are perfectly in accord with those obtained by aid of the *general*, empirical equation found by the author to hold *rigidly* for the average values of γ , even up to the critical temperature of benzene. This equation is

$$\gamma_{\text{C}_6\text{H}_6,t} = 2.115 \left(\frac{288.5 - t - 6}{(78/d_t)^{1/2}} \right),$$

where γ_t and d_t are the surface tension in dynes and density of benzene at the temperature of observation, t ; 78 is the molecular weight of benzene; 288.5 is its observed critical temperature; and 2.115 and 6 are constants. The density of benzene, for use in this formula, can be found up to 100° by aid of the relation $d_t = 0.9002 - 0.001066t$.

The equation for the work of any *one* observer alone is found to be identical with the above, except as to the value, 2.115, of the constant, which is slightly different for each observer, but *constant* throughout the temperature range studied by him. With a characteristic constant for each observer, in fact, this equation is found to give results which agree with the most remarkable accuracy with the observed values of $\gamma_{\text{C}_6\text{H}_6,t}$ of that observer at all temperatures (see Morgan, *Z. physik. Chem.*, 1915).

The *average* equation to give the *average* result of the surface tension of benzene of *all* observers, then, is the above, in which the *average* value of *all* the individual, slightly differing, constants is used, *i. e.*, 2.115.

Applying this form of equation to the drop weight results of benzene, from any one tip, *under the conditions discussed below*, it is found that the relationship

$$w_{\text{C}_6\text{H}_6,t} = K \left(\frac{288.5 - t - 6}{(78/d_t)^{1/2}} \right)$$

also represents with very great precision the drop weights in milligrams at various temperatures from that tip, *the value of K being constant and characteristic for any one tip, and independent of the temperature.*

Comparison of these two equations, for $\gamma_{\text{C}_6\text{H}_6,t}$ and $w_{\text{C}_6\text{H}_6,t}$ at every identical temperature, then, shows that, *independent of the temperature*, since all terms except γ , w , 2.115 and K would be identical

$$\frac{\gamma_{\text{C}_6\text{H}_6,t}}{w_{\text{C}_6\text{H}_6,t}} = \frac{2.115}{K} = \text{Constant},$$

for any one tip, t to have any desired value. In other words, Equation 1, as far as concerns the surface tension and drop weight of benzene from any one tip is thus shown to be rigidly true at all temperatures.

¹ THIS JOURNAL, 33, 1275-90 (1911).

constant $\times w_{l,t}$ have been most thoroughly investigated from the experimental and comparative point of view. In other words, it has been found experimentally just what conditions are necessary in order that, within the narrow limits of error of the drop weight estimation, the ratios $\frac{\gamma_{C_6H_6,t}}{w_{C_6H_6,t}}$, $\frac{\gamma_{H_2O,t'}}{w_{H_2O,t'}}$, and $\frac{\gamma_{l,t''}}{w_{l,t''}}$, where the sub-letter l represents *any* liquid, may be equal and constant in value, regardless of the values of t , t' and t'' ; or, what amounts to the same thing, that the values of $\gamma_{e,t'}$, as calculated from $\gamma_{l,t''} = \left(\frac{\gamma_{C_6H_6,t}}{w_{C_6H_6,t}} \right) w_{l,t''} = \left(\frac{\gamma_{H_2O,t'}}{w_{H_2O,t'}} \right) w_{l,t''} = \text{Constant} \times w_{l,t''}$, may agree with those found at that temperature by some other method. The latter form here, naturally, is the one employed directly in the drop weight method for surface tension, and at the same time leads, perhaps, to a more satisfactory test of the truth of the general relationship; for by aid of the equation giving the change in surface tension with the temperature (which can be readily found from its results at several temperatures), the values of γ_l at the various temperatures can be found by interpolation, and then compared with those found directly at those temperatures by the various other observers.

The conditions found necessary here, in few words, have to do with the *approximate* diameter of the dropping tip, and the drop weight and density, *i. e.*, with the volume of the drop on the tip. Whenever the above law holds, it is observed that the relation of drop volume to tip diameter is such that the drop forms with a "normal," bag-like profile, with sides which are parallel for at least a portion of their length. When the drop volume on the tip is so small that the drop runs rapidly to a point, and its sides are nowhere parallel, the law fails to hold; and the same is true when the drop volume for the tip is so large that the drop, at its lower extremity, bulges beyond an imaginary continuation of the walls of the tip.

At first glance it might seem, perhaps, that this imposed condition of "normal" drop profile would limit very materially the number of liquids which could be studied on any one tip; but actual experiment has shown that with *any* tip lying between certain approximate limits of diameter, the liquids excluded, by reason of abnormal drop volume, would be insignificant in number; and would only be those which possess drop volumes that are excessively small, *i. e.*, which have average or small surface tensions, accompanied by very high densities.

The purely experimental and comparative study, with various liquids, of a number of tips (17) lying in diameter between 3 and 8 mm. has shown that *for general purposes*, only those between 4.5 and 5.5 mm. leads to satisfactory results. *With any tip lying between these limits of diameter (4.5 and 5.5 mm.), however, it is found that the law holds rigidly, so long as the drop volume on the 4.5 tip is at least equal to 0.0196 cc., and on the 5.5*

to at least 0.0239 cc., any intermediate diameter giving a volume which is in simple proportion to the diameter of the tip. These limits include *ether*, with its very small surface tension of 15.3 dynes, and drop volumes of, respectively, 0.0196 and 0.0239 cc., as well as *water* (and probably also considerably higher values), with its almost maximum surface tension, 76 dynes, and very large drop volumes of 0.083 and 0.1 cc.

The study of carbon tetrachloride in this connection, with its average surface tension value of 24.9 dynes, but excessive density, 1.576, giving on the 4.5 tip a volume of but 0.0143 cc. shows that the minimum volume on that tip can be reduced to this value, *i. e.*, considerably below that for ether given above. This volume, 0.0143 cc., is apparently the lowest limit for the 4.5 tip, however, for with a larger tip, carbon tetrachloride, which is very satisfactory in behavior on the 4.5 tip, cannot be considered to lead to very satisfactory results. In the same way we find that 0.0239 cc. is the absolute minimum for satisfactory work on the 5.5 tip, for with ether any increase in diameter above that shows a failure of the law to hold rigidly. When all the possible abnormal liquids of the type of carbon tetrachloride are considered, *i. e.*, liquids of average or small surface tension, accompanied by excessively high densities, we see that the number of liquids excluded from the rigid holding of the law, for any tip lying between 4.5 and 5.5 mm. is indeed a *minimum*, which certainly would not amount to more than a very small fraction of 1% of all liquids. Any such liquid on these tips, giving a volume smaller than those indicated, however, must be excluded from use on these tips; although, naturally, a smaller tip, standardized by aid of a similar liquid, would lead to satisfactory results by the method.

Although actual, average tip diameters, have been given above, it will be noted that they are *not necessary for, or even used in, the calibration of the tip*, that being accomplished simply from the relationship of a γ value, as interpolated from observed results, and a w value, found experimentally, both being at some one, like, temperature.¹ To find the approximate diameter of a tip, to ascertain whether or not it lies between the given limits (which were accurately determined by aid of a dividing engine), a micrometer may be held above the tip, and results, usually too high by about 0.1 mm., obtained, or it may be found in millimeters, with an accuracy of about 0.1% by aid of the drop weight diameter of tip relation² for benzene at 27.8°, *viz.*, diameter = $\frac{w_{C_6H_6}}{5.37}$.

¹ It is possible that a misunderstanding on this point was the cause of the unjustified criticism of the method by Lohnstein (*Z. physik. Chem.*, 84, 410-18 (1913)), and of his "discovery" of a 4% discrepancy in its results. For a reply in detail to that criticism, see Morgan (*Z. physik. Chem.*, 89, 385 (1915)) in a paper referred to above which was accepted for publication early in 1914, and which although delayed by the war, should certainly appear as of an early date in 1915.

² See Morgan and Cann, *THIS JOURNAL*, 33, 1065 (1911).

In connection with the tip diameter, it will be realized that there must be some one diameter which would give a value of the "Constant" in (1) and (2) equal to unity; in which case the measured drop weight in *milligrams* would also be the surface tension of that liquid, at that temperature, in *dynes*. This diameter can be calculated by first finding $\gamma_{C_6H_6}$ at 27.8° from the $\gamma_{C_6H_6,t}$ relationship, and then substituting that for $w_{C_6H_6}$ in the equation for the "diameter," and solving for that. The value thus found is 5.01 mm. Such a tip would save considerable time in the calculations, but such difficulty would probably be encountered in obtaining it of *just* that diameter, that it is better to do as has been done in the past, and employ a tip possessing a "Constant" which is either somewhat larger or smaller than unity, the actual diameter of which is known only approximately.¹

The above is a brief sketch of the method for the determination of surface tension from the drop weight which has been developed as the result of the series of investigations mentioned above. *For SEVENTY of the ONE HUNDRED specially purified liquids, for which the surface tension was known, liquids of every type and giving all possible values of drop volume within the given limits, the above equations, (1) and (2), have been found to hold rigidly, between the tip diameters of 4.5 to 5.5 mm., the calculated surface tensions agreeing with some value as found at the same temperature by the capillary rise method, within a few tenths of 1% at worst. And the same can be said of all the TEN solutions, for which surface tension results were at hand.*

In the case of the other thirty liquids for which the surface tensions were known, however, the agreement was not so good; in some few cases being worse than that usually found among the results of different workers on the same liquid by the same (capillary rise) method. These liquids in many cases were those which are difficult to obtain, or then to retain, in the pure state; in which case in *this* work, the liquid was redistilled or purified in some other way immediately before each drop weight measurement was made; *second*, some of these liquids had been studied by only one observer of capillary rise, and in a number of cases the results of this observer for other liquids were consistently either higher or lower

¹ The values for the "Constant" of the 4.5 tip is found to be 1.109, and that for the 5.5 to be 0.910; and the mean of these would also give constant = 1 for a tip of 5 millimeters.

The values of the "Constant," naturally, can also be employed to calculate the average diameter of the tip with an accuracy of about 0.1%, the value of the "Constant" being inversely proportional to the diameter of the tip. In this way we would have:

$$4.5 : \text{diameter} :: \text{"Constant"} : 1.109$$

or

$$5.5 : \text{diameter} :: \text{"Constant"} : 0.910$$

This is indeed the simplest and best method.

than those of other observers by the same method; *third*, none of these liquids showed any variation from the "normal" drop profile, and further, none possessed any property that was not possessed to the same or a greater extent by other liquids which gave satisfactory agreements.

For the above reasons it is considered that the comparison in the case of these thirty liquids *cannot as yet be considered as final*, for until surface tensions, which are known to be *accurate*, are at hand, it must be assumed that it is the fault of the values of this property, that the method which gives such precise results for the *seventy* liquids should suddenly and inexplicably give less precise values for the thirty liquids, which differ from them in no single property that could affect the relationship.

Ferguson,¹ after recognizing the precision of this method, and rightly criticizing the various attempted *theoretical* derivations of a drop-weight—surface tension law (which in all cases have been found to be in disagreement with the experimental results published from this laboratory)² brings up the question as to whether or not the drop weight method is affected by the so-called angle of contact, thought to affect the capillary rise method, but not others. The only answer that can be made to this question, as he recognizes, is that based upon experiment. Unfortunately, however, there are not enough data at hand from any method for surface tension other than that of capillary rise, which are sufficiently concordant to standardize and then test with precision any empirical relationship between these surface tensions and the drop weights at the same temperature. Until such data are at hand, and until the effect of the angle of contact is studied sufficiently to show that it *does* have any effect upon capillary rise, upon which at present there is no general agreement, we can only assume, from the seventy cases above, that the angle of contact either exerts a very small influence on the capillary rise results, and the drop weight method is not affected by it; or, that both methods are affected by it in the same way. There is no reason for assuming, as far as can be seen, that the seventy liquids are just those for which the angle of contact is nearly zero, while it has a larger value for the thirty; and that consequently the drop weight not being affected by it, *should* only agree in those cases where the angle is zero.

Until more definite information as to the angle of contact is at hand, the experimental results from this laboratory can only be taken as showing that the drop weight and surface tension, *as found by the capillary rise method*, are proportional.

NEW YORK, N. Y.

¹ *Science Progress*, No. 35, Jan., 1915.

² See Morgan, *Z. physik. Chem.*, *loc. cit.*

A METHOD OF REDUCING SOME METALS IN CRYSTALLIZED FORM ON GLASS SLIPS AS PERMANENT MICROSCOPE MOUNTS.

By JAS. H. BOWMAN.

Received April 10, 1915.

The process applies to such metals as are reducible from solution by some other metal.

For some years I had intermittently attempted the deposition of gold and silver in the crystallized forms known as fern and moss figures on glass slips for use as microscopic objects and had been partially successful. Finally I happened upon a method that gave quite satisfactory results in respect to both the perfection of the figures and the permanency of the mounts.

The metal with which I first obtained success was silver and the method used will indicate a general process which may be applied with variations in manipulation to gold, antimony, copper, bismuth, cadmium, tin, lead, etc., each metal requiring some modification of the treatment peculiar to itself.

Silver Crystals.—A solution is prepared by dissolving silver nitrate in distilled water—1 to 10—and adding an equal quantity of a concentrated solution of zinc nitrate. A small drop of the mixed solution is placed on a chemically clean glass slip and spread by drawing the end of another slip backwards and forwards over it until a thin film covers the desired portion of the slip. Then on filing a piece of metallic zinc in such manner that the filings fall thinly and somewhat evenly over the moist surface, reduction of the silver begins at once, each particle of the zinc becoming a center of crystallization as shown in Plate 1, Fig. 1. The zinc nitrate was introduced to prevent the drying of the solution by evaporation before the reduction of the silver becomes complete. The slip is placed, moist side upward, on a piece of damp filter paper and covered with a bell jar. Under the jar the moist atmosphere retards drying until crystallization is completed, which usually takes from 15 to 20 minutes. The slip is removed and allowed to dry in the air, not completely, however, as incrustations will form on the crystals—but until nearly dry. At this stage a few drops of a thin solution of Canada balsam in xylol, introduced at the side, is run over the preparation, the slide being slanted to allow the balsam to reach every part of the surface. It is then set aside to dry in a dust proof atmosphere.

In an hour or two it may be covered in the usual way practised with balsam mounts. The thin solution of balsam holds the delicate crystals of silver against disruption by the final covering and mounting process.

From the zinc centers radiating, fern-like, crystals spring. If the solution be too deep on the slip the reduced silver will remain an amor-

phous mass but with a filmy solution the fern-like crystals will be very beautiful, and have a bright metallic luster. If the zinc particles are too sparsely spread, silver nitrate will remain in solution and will, by reduction, blacken the balsam. This does not in any way impair the beauty of the slide as the black gives a good background for the crystalline centers of metals.

Gold Crystals.—Both fern-like and filamentous crystals of this metal are obtained by reducing gold chloride by zinc. A saturated solution of gold chloride is made and slightly acidulated with hydrochloric acid mixed with an equal quantity of concentrated solution of zinc chloride. A very small drop is placed on a cleaned slip and then treated in the manner described for silver. The areas of crystal growth should be close together, otherwise in the spaces amorphous gold will be reduced by the balsam and will give the mount a blemished appearance. The crystals form in about the same time as in the case of silver. If wire gold crystals are desired a very thin film of solution only must be used; by deepening the film, fern-like forms are obtained.

Copper Crystals.—The solution should be composed of a cold saturated solution of copper sulfate mixed with an equal part of concentrated solution of zinc chloride and acidulated slightly with hydrochloric acid. Treat as for silver above. In drying, there is a strong tendency to the formation of a green incrustation which ruins the mount, hence it is advisable to add the thin balsam solution while the mount is still quite moist. If time be not allowed for complete reaction, bubbles of hydrogen are formed and interfere with the perfection of the mount.

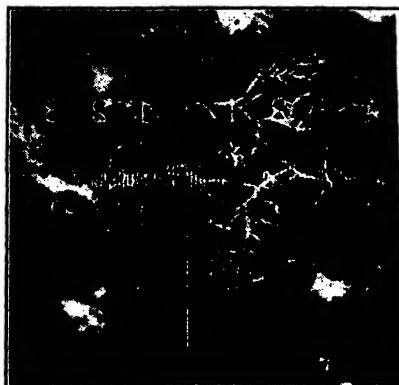
Lead Crystals.—A concentrated cold solution of lead acetate is mixed with an equal quantity of a 25% solution of glycerin in water. The subsequent procedure is similar to that for the other metals. There are two reasons for using glycerin. It prevents too rapid drying and the incrustation of the crystals and further it promotes the solubility of the difficultly soluble lead compound which is precipitated during the process. I do not know of any other agent than glycerin that will prevent the incrustation referred to. It should be noted that unless the crystal centers are close together resolution of the crystals is liable to take place.

Bismuth Crystals.—A concentrated solution of bismuth chloride is mixed with 25% of glycerin, treated as in the other cases. There is a tendency in this case for the reduced metal to be black and amorphous. It is a question of proper acidity which must be determined by trial.

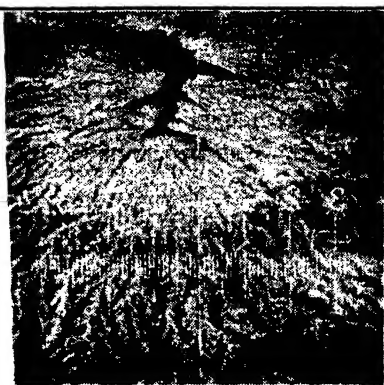
Tin Crystals.—A concentrated solution of tin chloride mixed with an equal quantity of solution of zinc chloride, treated as in the case of silver.

Cadmium Crystals.—Proceed as in the case of tin.

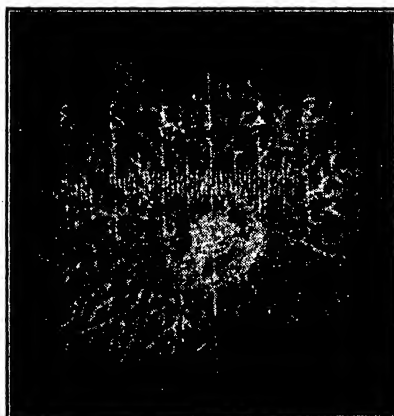
The crystal clusters formed by this method have the reducing particle of zinc left in the center. This objection cannot be very well avoided.



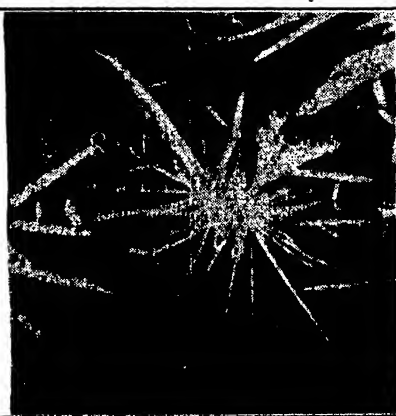
Silver.



Gold.



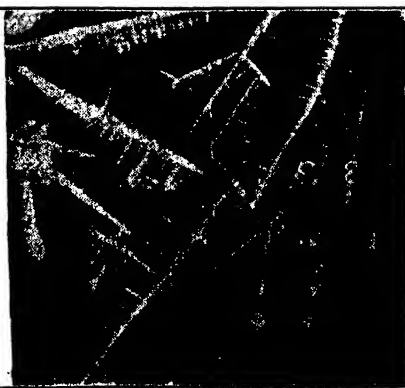
Copper.



Lead.



Bismuth.



Tin.

During the process some of the zinc seems to be carried into the crystals, suggesting that the purity of the metal of the crystals increases as it gets further from the center. This is very noticeable in the examples of both gold and copper.

The crystals from these metals differ much in their branching and curving tendencies. In tin, the crystals are straight and the side growths are at right angles. Lead crystals show less tendency to side branching and curve but little. In gold, as well as in some of the other metals, the branching is quite arborescent. Are the crystals of tin an illustration of compounding by relay?

The crystals formed by this method are well represented in the accompanying plates—they are of some scientific interest and form brilliant microscopic objects when viewed by reflected light.

I owe the microphotographs to the kindness of Mr. J. T. Burt-Gerrans, of the University of Toronto. Each small division of the scale corresponds to 0.015 mm. on the slide.

LONDON, ONT.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK CITY.]

A NEW TEST FOR COPPER.¹

BY W. G. LYLE, L. J. CURTMAN AND J. T. W. MARSHALL.

Received March 18, 1915.

Introduction.

The test to be described in this paper is based on the insolubility of the copper salt of α -amino-*n*-caproic acid ($\text{CH}_3(\text{CH}_2)_4\text{CHNH}_2\text{COOH}$). Kudielka,² in 1908, prepared this acid and its copper, nickel and cobalt salts and determined their solubilities in water. In the course of their work on the quantitative determination of amino acids, Kober and Sugiura³ state that the insoluble complex which *n*-aminocaproic acid forms with copper may be useful in analytical work.

Some preliminary work on the part of the authors indicated that an aqueous solution of *n*-aminocaproic acid was an exceedingly valuable reagent for the detection of small amounts of copper. It was the object of this investigation to ascertain the most favorable conditions for the use of this reagent and to determine its applicability to solutions of salts of foreign metals containing small amounts of copper.

The reagent was prepared from commercial *n*-caproic acid by the method proposed by Abderhalden, Fuchs and Froehlich⁴ and further purified

¹ Read before the New York Academy of Sciences, March 15, 1915, and the New York Section of the American Chemical Society, April, 1915.

² *Monatsh.*, 29, 351 (1908).

³ *THIS JOURNAL*, 35, 1584 (1913).

⁴ *Z. physik. Chem.*, 86, 455 (1913).

through its copper salt. The solution used throughout our work was prepared by dissolving 0.67 g. of the acid in 100 cc. of water; the mixture was heated to facilitate solution and then filtered.

It was found that the precipitation of copper by aminocaproic acid was influenced considerably by the presence of free mineral acid. Since mineral acid is liberated as a by-product of the reaction, it was decided to employ a buffer in making the test. For this purpose a 40% solution of sodium acetate was found satisfactory.

The pure copper salt of *n*-aminocaproic acid was prepared. Evaporation of 1000 cc. portions of an aqueous solution of this compound gave residues from which the solubility of the salt at 18° was calculated to be of the order of 1 in 100,000.¹

Determination of the Sensitiveness of the Test.—By means of a graduated pipet definite amounts of a standard copper nitrate solution were introduced into a series of test tubes. 1 cc. of 40% sodium acetate and 1 cc. of aminocaproic acid solution were then added, the contents of the tubes shaken and allowed to stand. The results obtained are shown in Table I.

TABLE I.

Total Vol., 3 cc.; 1 cc. of 40% $\text{NaC}_2\text{H}_3\text{O}_2$; 1 cc. of Reagent.

| No. | Mg. Cu. | Result. |
|--------|---------|--|
| 1..... | 1.000 | Immediate grayish blue precipitate. |
| 2..... | 0.500 | Immediate grayish blue precipitate. |
| 3..... | 0.010 | Slight white precipitate. |
| 4..... | 0.005 | Faint precipitate at end of 5 minutes. |
| 5..... | 0.004 | Fair test in 5 min.; much better in 12 minutes. |
| 6..... | 0.003 | Faint test in 5 min.; (limit) much better in 12 min. |
| 7..... | 0.002 | Negative test in 5 min.; faintly positive in 12 min. |
| 8..... | 0.001 | Negative test in 12 min. |
| 9..... | 0.000 | Negative test in 12 min. |

Comments.—The above experiments were repeated a number of times with the same results. The limit of the test in 5 minutes (0.003 mg. Cu in 1 cc. of the original solution) represents a concentration of 1 part in 333,000. While it requires some practice to recognize the test given by 0.003 mg. of copper, decided and unmistakable results are obtained with 0.004 mg. The precipitate has a tendency to agglutinate, to rise to the surface of the liquid and to creep up the walls of the tube when the latter is gently shaken. This characteristic property of crawling up the sides of the containing vessel makes possible the recognition of smaller amounts of precipitate than would be the case if the precipitate remained in suspension or settled to the bottom of the container. The "crawl" is best seen by gently shaking the tube and viewing it in good light against a

¹ Kudielka (*Loc. cit.*) found the solubility of the copper salt to be 3.6 parts in 100,000 at 23°.

dark background. In some of the preliminary tests with 0.004 mg. Cu, negative results were obtained. An examination into the causes showed that the greasy condition of the tubes prevented the precipitate from crawling. It is therefore imperative in making the test to have the tubes scrupulously clean. This was accomplished by first scrubbing with soap solution, rinsing, then treating with hot chromic acid mixture and finally rinsing a number of times with distilled water. The solutions to be tested for copper were always carefully examined for any particles in suspension that might be mistaken for a positive test and if not absolutely clear, the solution was filtered before adding the reagent.

A comparison of the sensitivity towards copper of *n*-aminocaproic acid and synthetic leucine was then made. A solution of Kahlbaum's synthetic leucine of the same strength as our reagent (0.67%), failed to give a precipitate with amounts of copper smaller than 0.03 mg. Thus the normal acid will detect about one-tenth the quantity of copper that can be recognized with the iso-derivative. The presence of moderate amounts of the iso-derivative was found to materially diminish the sensitivity of the reagent.

Behavior of the Reagent with Other Metals.—Having determined the limit of the test in solutions containing copper alone, our next step was to ascertain whether there were any other metals which would give the test. To this end, 1 cc. of a solution containing 100 mg. of the metal as nitrate or chloride was treated with 1 cc. of 40% sodium acetate solution and 1 cc. of aminocaproic acid. *Of all the common metals, zinc and mercury alone gave precipitates.* The test given by zinc under these conditions was very faint, but by diminishing the quantity of zinc to a few milligrams, surprisingly strong reactions were obtained.

This anomalous behavior of zinc salts necessitated a repetition of the above experiments with small quantities (1–10 mg.) of each of the metals. The results showed that mercury and zinc alone gave precipitates and therefore interfere with the test for copper. Methods for overcoming these interferences were devised and will be given later when these metals are considered.

Whether or not the presence of large amounts of foreign metals would interfere with the detection of relatively minute quantities of copper was the next point investigated. The general procedure was as follows:

To 1 cc. of the solution containing 100 mg.¹ of the foreign metal, 0.1 cc. of copper nitrate solution containing 0.01 mg. of Cu was added. To this mixture, 1 cc. of 40% sodium acetate and 1 cc. of aminocaproic acid were added. A control was run at the same time and in every case the results were checked by repeating the experiment. Following this pro-

¹ Because of the relatively small solubility of AlCl_3 , 2 cc. of solution were required to supply 100 mg. of Al.

cedure, good tests were obtained in the presence of Pb, Cd, Ni, Co, Mn, Ba, Sr, Ca and Mg, respectively. With lead solutions, a finely divided precipitate appeared in the controls at the end of 10 minutes, though they were perfectly clear at the end of 5 minutes. For this reason it was decided to remove the greater part of the lead with 1 cc. of 20% NaCl solution. After washing the precipitated lead chloride with 1 cc. of cold water, good tests and perfect controls were obtained.

Interferences.—It was thought that substances which form only slightly ionizable complexes with copper would interfere with its precipitation by aminocaproic acid. Experiments showed that an excess of KCN inhibits the test. In Table II the influence of ammonium salts is shown.

TABLE II.

Total Volume, 3 cc.; 1 cc. of 40% $\text{NaC}_2\text{H}_3\text{O}_2$; 1 cc. of the Reagent.

| No. | Mg. Cu. | | Result. |
|----------|---------|--------------------------------------|-------------------------|
| 1-2..... | 0.004 | 0.6 cc. 50% NH_4NO_3 | Negative in 10 hours. |
| 3-4..... | 0.004 | 0.6 cc. 30% NH_4Cl | Negative in 10 hours. |
| 5-6..... | 0.004 | | Good test in 5 minutes. |

Smaller amounts of ammonium salts were found to retard the formation of a precipitate. Substances containing amino groups were also found to interfere. Thus negative tests for 0.01 mg. Cu were obtained in the presence of 10 mg. of each of the following substances: Glycocoll, synthetic leucine, glycyl glycine, "Seiden peptone" and casein.

Sodium citrate was also found to interfere; but contrary to expectations good tests were obtained with 0.004 mg. Cu in the presence of relatively large amounts of tartrates.

The interference due to ammonium salts and organic matter may readily be removed by ignition.

Special Procedures.

Silver.—The addition of 1 cc. 40% sodium acetate solution to 1 cc. of a 10% Ag solution causes the precipitation of silver acetate. In the absence of sodium acetate, a test was not obtained with 0.01 mg. Cu in the presence of 1 cc. of 10% silver solution. It was therefore necessary to remove the silver before the test could be applied. This was accomplished by means of sodium chloride. The results of the experiments appear in Table III.

TABLE III.

Total Volume before Precipitating with 1 cc. 20% NaCl, 1.1 cc. To Filtrate Added
1 cc. 40% $\text{NaC}_2\text{H}_3\text{O}_2$, 1 cc. Reagent.

| No. | Mg. Ag. | Cu. | Result. |
|----------|---------|------|----------|
| 1-2..... | 100 | 0.00 | Negative |
| 3-4..... | 100 | 0.01 | Good |

Bismuth.—A solution of $\text{Bi}(\text{NO}_3)_3$ in 10% conc. HNO_3 containing 100 mg. of the metal per cc. was used. One cubic centimeter of this

solution was found to be too acid to yield a precipitate in the presence of copper. The procedure which gave satisfactory results was as follows:

To 1 cc. of the bismuth solution 0.01 mg. of copper was added. The solution was then diluted to 20 cc. This caused a separation of basic salt. After standing for several minutes, 2 cc. NH_4OH (1-1) were added drop by drop and the mixture was filtered. The filtrate and washings were evaporated to a few drops,¹ taken up with water, filtered again through a very small filter and then treated with 1 cc. of sodium acetate and 1 cc. of the reagent. Good results were obtained in 5 minutes.

Antimony.—A 10% solution of antimony as chloride was used. The method employed was similar to that described above for bismuth. Good tests and controls were obtained.

Tin.—A solution of SnCl_4 containing 100 mg. Sn in 1 cc. was employed in all our tests with this metal. 1 cc. of this solution yields a precipitate when treated with 1 cc. of 40% sodium acetate. By precipitating the tin with NH_4OH or 40% $\text{NaC}_2\text{H}_3\text{O}_2$, nearly all the copper originally added either combined with, or was adsorbed by, the precipitate. This was shown by the blue color of the precipitate. We were unable, moreover, after repeatedly washing the precipitate with either water, or dilute NH_4OH , to get a test for copper in the combined filtrate and washings after concentration to 0.5 cc. when less than 0.1 mg. of Cu was originally present. By removing the ammonium salts from the filtrate, the test was rendered more delicate, but 0.02 mg. of copper always escaped detection. As nickel does not interfere with the test, it was thought that by adding a small amount of this metal (2-10 mg.) to the solution of copper and tin, it would be possible by means of an excess of potassium hydroxide to precipitate the copper with the nickel and thus keep all the tin in solution. This procedure, however, failed to detect 0.05 mg. of copper for the reason that the precipitated nickel adsorbed some tin which could not be washed out and which interfered with the final test. Based on the volatility of stannic chloride in hydrochloric acid solution, a method was found which yielded uniformly satisfactory results. The solution containing the tin and copper was treated with HCl and evaporated *just to dryness*: more HCl was then added and the solution again evaporated. After the third evaporation, 1 cc. of water was added and the solution treated with 1 cc. of 40% $\text{NaC}_2\text{H}_3\text{O}_2$ and 1 cc. of the reagent. The results are shown in Table IV.

TABLE IV.

| No. | Mg. Sn. | Mg. Cu. | Result. |
|----------|---------|---------|--------------|
| 1..... | 100 | 0.100 | Strong test. |
| 2..... | 100 | 0.010 | Strong test. |
| 3..... | 100 | 0.006 | Good. |
| 4-5..... | 100 | 0.000 | Negative. |

¹ By removing the ammonium salts at this point, better results may be obtained.

Zinc.—Table V gives the results obtained with solutions of zinc of strength 100 mg. in 1 cc.

TABLE V.

Volume before the Addition of Reagent, 1.1 cc.; 1 cc. of 40% $\text{NaC}_2\text{H}_3\text{O}_2$; 1 cc. of Reagent.

| No. | Mg. Zn. | Mg. Cu. | Results. |
|----------|-----------------------------------|---------|------------------------|
| 1-2..... | 100 as $\text{Zn}(\text{NO}_3)_2$ | 0.01 | Precipitate. |
| 3..... | 100 as $\text{Zn}(\text{NO}_3)_2$ | 0.00 | Precipitate. |
| 4..... | 100 as ZnSO_4 | 0.00 | Precipitate. |
| 5-6..... | 200 as ZnSO_4 | 0.10 | Immediate precipitate. |
| 7-8..... | 200 as ZnSO_4 | 0.00 | Negative in 1 hour. |

These results find their explanation in the acidity contributed by the zinc salt. 200 mg. of Zn gave a higher hydrogen ion concentration to the solution than that given by 100 mg. and as a consequence no precipitate was obtained in Experiments 7 and 8. If this explanation be correct, 1 mg. of Zn should give a better test than 100 mg. Experiments showed not only that this was the case, but also that *n*-aminocaproic acid is a fairly sensitive reagent for the detection of small amounts of zinc as shown in Table VI.

TABLE VI.

Solution ZnSO_4 . 1 cc.; 1 cc. of 40% $\text{NaC}_2\text{H}_3\text{O}_2$; 1 cc. of Reagent.

| No. | Mg. Zn. | Result. | | |
|----------|---------|-----------|-----------|---------------------|
| | | 1 min. | 2 min. | 5 min. |
| 1..... | 0.05 | Good. | Strong. | Strong. |
| 2..... | 0.03 | Negative. | Good. | Very good. |
| 3..... | 0.02 | Negative. | Negative. | Very faint (limit). |
| 4-5..... | 0.01 | Negative. | Negative. | Negative. |

The results in Table VI show that under the conditions employed in testing for copper, the reagent is capable of detecting 0.02 mg. of zinc. Since the reagent is sensitive to small quantities of zinc, there was need for a means of differentiating between zinc and copper if the test were to be applied to unknown solutions. After some experimentation, it was found that zinc does not precipitate when the hydrogen ion concentration (*p*-nitrophenol as indicator) exceeds $10^{-5.5}$. If to an acid solution of zinc containing aminocaproic acid and a drop of *p*-nitrophenol solution (0.04%), sodium acetate be added, a yellow color will develop which deepens on further addition of acetate. When the color is only a faint yellow, ($\text{C}_\text{H}^+ = 10^{-5.2}$) no zinc will come down. Not until sufficient sodium acetate has been added to give a strong yellow color ($\text{C}_\text{H}^+ = 10^{-5.8}$) will the zinc precipitate in 5 minutes. The results in Table VII show the reliability of the method.

TABLE VII.

Volume, 2 cc.; One Drop *p*-Nitrophenol; Adjusted to Light Yellow Color with Sodium Acetate and 0.1 *N* HCl; 1 cc. Reagent.

| No. | Mg. Zn. | Mg. Cu. | Result. |
|-----------|---------|---------|------------------------|
| 1-5..... | 1.0 | 0.000 | Negative in 5 minutes. |
| 6-10..... | 1.0 | 0.004 | Positive in 5 minutes. |

Mercury.—The following solutions were used in the experiments with mercury, *viz.*: Solution A, Hg 10% (as nitrate) in 2% conc. HNO_3 ; Solution B, Hg 10% (as chloride) in 5% NaCl solution;¹ Solution C, Hg 1% (as chloride) in H_2O .

1 cc. each of solutions A, B and C was treated with 1 cc. of 40% $\text{NaC}_2\text{H}_3\text{O}_2$ and 1 cc. of the reagent. A fair test was obtained with solution A, B was negative, while solution C gave a strong test.

These results indicated that the presence of NaCl prevented the precipitation of the mercury. To further test this conclusion the following experiments were made:

TABLE VIII.

Volume after the Addition of 1 cc. of 40% $\text{NaC}_2\text{H}_3\text{O}_2$, 3 cc.; 1 cc. of the Reagent.

| No. | Mg. Hg. (Sol. A). | Mg. Cu. | 20% NaCl cc. ² | Result. | |
|------------|----------------------|---------|---------------------------|----------------------|---------|
| | | | | 5 min. | 10 min. |
| 1..... | 100 | 0.00 | 0.0 | + | + |
| 2-5..... | 100 | 0.00 | 1.0-0.5 | — | — |
| 6-8..... | 100 | 0.01 | 1.0-0.5 | + | + |
| 9..... | 1 | 0.00 | 0.0 | Immediate heavy ppt. | |
| 10-11..... | 1 | 0.00 | 0.5-0.1 | Negative. | |

TABLE IX.

Experiments with HgCl_2 solutions. 1 cc. 40% $\text{NaC}_2\text{H}_3\text{O}_2$; 1 cc. Reagent.³

| No. | Mg. Hg. (Sol. B). | Mg. Cu. | 20% NaCl cc. | Result. |
|----------------------|----------------------|---------|-----------------|----------------------|
| 1-2..... | 100 | 0.00 | 0.0 | — |
| 3-4..... | 100 | 0.01 | 0.0 | + |
| 5 ⁴ | 1 | 0.00 | 0.0 | Immediate heavy ppt. |
| 6 ⁵ | 1 | 0.00 | 0.5 | Negative in 10 min. |
| 7 ⁵ | 1 | 0.00 | 0.1 | Negative in 10 min. |

The results of the table show that the addition of NaCl will prevent the formation of basic salt or aminocaproate in solutions of mercury. Before concluding our work with this metal we determined that small amounts may also be prevented from precipitating by regulating the acidity as in the case of zinc.

Iron and Aluminum.—In the presence of 100 mg. of either of these metals in the form of chlorides, we were unable to get positive tests with

¹ The NaCl was added to increase the solubility of HgCl_2 .

² The addition of NaCl to the Hg solution causes the formation of an exceedingly faint cloud, due probably to HgCl_2 in suspension. The solution clears up somewhat on the addition of the aminocaproic acid. However, in no case was this cloud found to interfere with the test. In the many experiments made, the controls never showed the characteristic "crawl;" while in the presence of copper decided tests were obtained.

³ In tests 1-4 the volume of the solution before the addition of the reagent was 2 cc.

⁴ In tests 5-7 the volume of the solution before the addition of the salt was 1 cc.

⁵ At the end of 10 minutes, 9 mg. of Hg were added slowly from a pipet to these tubes. No precipitate formed in 10 minutes.

0.05 mg. of copper or less. This is due to the fact that before the acidity can be depressed sufficiently to permit the precipitation of small amount of copper (Cu^{2+} about 10^{-4}) these metals (also Cr) separate in the form of hydroxides and mask the reaction. After much experimenting the following procedure was found efficient: 100 mg. of Fe or Al in the form of their chlorides were mixed with 0.05 mg. Cu as nitrate. The mixture, the volume of which was about 2 cc., was slowly poured with constant stirring into 3 cc. NH_4OH (1-1); the solution was filtered through a fluted filter and the precipitate washed with 2 cc. of water. The combined filtrate and washings were evaporated to dryness and the ammonium salts removed by heating with KOH. The solution was then made acid with HCl, evaporated to one drop, taken up with 1 cc. of water, and tested in the usual manner. By this procedure good tests were consistently obtained in 3 minutes.

Chromium.—A 10% solution of Cr as $Cr(NO_3)_3$ was used in this work. 1 cc. of this solution to which 0.05 mg. of copper were added failed to give the test. Precipitation with NH_4OH , as in the procedure for Fe and Al, did not serve in this case, owing to the appreciable solubility of $Cr(OH)_3$ in ammonia. The filtrate always contained sufficient chromium to confuse the test.

To determine whether the oxidation of the chromium to chromic acid would eliminate the interference of this metal, tests were made for copper in the presence of K_2CrO_4 . The results showed that 100 mg. of Cr as chromate did not prevent the precipitation of 0.01 mg. of Cu. Subsequent experiments, however, starting with the metal as nitrate and oxidizing to chromate with sodium peroxide did not give consistent results.

After oxidation it was necessary to make the mixture acid in order to keep the copper in solution. In this connection a difficulty was encountered in attempts to adjust the acidity; for the test, even when 1 cc. of 40% sodium acetate is used, cannot be applied if the initial acidity is too great. Again, the strong color of the chromate solution does not permit the use of the indicator, without which it would be impossible in an unknown solution to determine whether the test were due to the presence of copper or zinc. It was, therefore, necessary to remove the CrO_4 . The chromate was dissolved in about 10 cc. of water, 1 cc. of NH_4OH (1-1) added, the mixture heated to boiling and an excess of $BaCl_2$ added. This procedure appeared sound, first because the presence of barium would not interfere with the test, and second, because $BaCrO_4$, being crystalline, would not adsorb appreciable quantities of copper. The filtrate from the $BaCrO_4$ was evaporated just to dryness, taken up with 1 cc. of water and refiltered through a very small filter into a test tube. 1 drop of *p*-nitrophenol was then added, the acidity adjusted to a faint yellow and 1 cc. of the reagent added. The following results were obtained:

| No. | Mg. Cr as K_2CrO_4 . | Mg. Cu. | Mg. Zn. | Results. |
|--------|---------------------------|---------|---------|-------------------------|
| 1..... | 100 | 0.05 | 0.0 | Good test in 1 min. |
| 2..... | 100 | 0.00 | 0.1 | Negative test in 5 min. |

At the expiration of 5 minutes the contents of Tube 2 were divided into two portions. 0.02 mg. of Cu added to one portion gave a good test, showing that the conditions were favorable for the precipitation of copper. To the other portion 0.1 *N* NaOH was added till a strong yellow color developed. A copious precipitate was then obtained, showing the presence of zinc.

Nickel and Cobalt.—The reagent is capable of detecting 0.01 mg. of copper in the presence of 100 mg. of either of these metals.¹ Although the aminocaproates of nickel and cobalt are fairly insoluble,² these salts are not formed under ordinary conditions when $C_H^+ > 10^{-7}$. Thus they are much more sensitive to acid than the corresponding zinc salt and, consequently, conditions permitting the differentiation between copper and zinc will completely prevent the precipitation of nickel and cobalt. Although the results showed that under our conditions (1 cc. 40% sodium acetate³ as buffer) nickel and cobalt remained in solution, a small decrease in the hydrogen ion concentration, such as might be caused by a trace of alkali in the sodium acetate or by heating the mixture, would bring about a slight precipitation of these metals. Consequently, in an unknown solution, when 1 cc. of 40% sodium acetate is used as a buffer, a positive test cannot be regarded as conclusive for copper, because of the possible presence not only of zinc but also of nickel and cobalt. The strong color of solutions of nickel and cobalt precludes the use of *p*-nitrophenol as an indicator for adjusting the acidity. We know of no feasible method whereby a separation of 0.01 mg. of copper from 100 mg. of nickel or cobalt can be effected. We therefore recommend in such cases the following procedure. To the neutral or faintly acid solution add 1 cc. of 40% sodium acetate and 1 cc. of aminocaproic acid. Allow the mixture to stand for about one-half hour.⁴ The precipitate, which may consist of aminocaproates of Cu, Zn, and traces of Ni and Co, is collected on a small filter, thoroughly washed, and then dissolved in hot dilute HCl. The filter is well washed, the combined solution and washings concentrated, *p*-nitrophenol added, the acidity adjusted to a pale yellow, and finally 1 cc. of aminocaproic acid added. A precipitate proves the presence of copper. Following this procedure, good tests were obtained

¹ With some preparations of the nitrates of nickel and cobalt, only very faint tests were obtained in 5 minutes; on standing for 10 or 15 minutes, however, the tests improved decidedly.

² According to Kudielka (*Ibid.*), the solubility of the nickel salt is about 29 parts in 100,000; that of the cobalt salt is 21 parts in 100,000.

³ Kahlbaum's zur Analyse.

⁴ This is to insure complete precipitation; frequent agitation is advantageous.

from solutions containing 0.02 mg. of copper and 50 mg. of nickel or cobalt in a volume of 1 cc. In the absence of copper, this method gave good controls.

Procedure for Unknowns Containing all Metals.—We do not know of a systematic procedure whereby any of the sensitive reagents hitherto employed for the detection of minute amounts of copper can be applied to solutions containing all the common metals. The great difficulty encountered in such cases is to be found in the tendency of precipitates, particularly those of a gelatinous character, to adsorb appreciable quantities of copper. Based on our experience with the test when applied to the metals individually, we would suggest the following procedure, observing the precautions necessary in quantitative work. After the removal of the silver group by means of HCl, the filtrate and washings are treated with an excess of KOH, heated and filtered. The precipitate is then dissolved in HCl and evaporated to a few drops. More HCl is added and the solution again evaporated to a few drops. The diluted solution is then poured into an excess of NH_4OH and filtered. The filtrate is evaporated to dryness and boiled with KOH to remove ammonium salts. The solution is then acidified with HCl and heated to dissolve the CuO .¹ 1 drop of *p*-nitrophenol is added, the acidity adjusted and test applied.

Remarks Concerning the Comparative Merits of the Reagents for Copper.—*N*-Aminocaproic acid possesses an important advantage over all the other reagents used for the detection of small amounts of copper in that, when the simple precautions to avoid the interference of zinc or mercury are taken, the test is highly characteristic and specific for copper.

It appears to be more delicate than the ammonia test according to the figures given by Pritz, Guilanden and Withrow,² and it possesses the further advantage that the interference of nickel may be readily overcome. Experiments with 0.004 mg. of copper gave decided tests with *n*-aminocaproic acid, but with ferrocyanide the tests were not evident except when compared with the blank; moreover, with ferrocyanide, the color, even with considerable amounts of copper, could not be distinguished from that of the control when examined at night. Again with the ferrocyanide test there are many more metals which interfere than is the case with aminocaproic acid. Solutions containing amounts of Fe, Ni, Co, Pb, Cd, Mn small enough to permit the use of an indicator may be tested directly with aminocaproic acid. Thus the almost universal presence of traces of iron, which would prevent the direct use of the ferrocyanide test, will

¹ If the solution is colored, and the indicator cannot be satisfactorily employed, recourse must be had to the procedure recommended for Ni and Co.

² THIS JOURNAL, 35, 168 (1913).

not interfere in the least with the aminocaproic acid test. Ammonium sulfide has¹ also been recently shown to be an exceedingly sensitive reagent for copper, but the large number of metals which interfere materially limits its usefulness. At the present time the cost of *n*-aminocaproic acid greatly exceeds that of the other reagents, but it is believed that its great usefulness will serve to cheapen it considerably. It is moreover a simple matter to recover the acid from waste solutions; so that the same supply can be used repeatedly.

Experiments are now in progress in this laboratory to determine the behavior of the rarer elements with *n*-aminocaproic acid and also the conditions under which the reagent may be applied as a specific test for zinc. The use of this reagent for the purposes of quantitative analysis is also under consideration.

Summary.

1. It has been shown that an aqueous solution of normal aminocaproic acid is an exceedingly sensitive reagent for the detection of copper. With this reagent 0.004 mg. of copper may be detected with certainty.

2. Mercury and zinc are the only other common metals which yield, under the conditions specified, a precipitate with the reagent. The interference of the former may be overcome by the addition of sodium chloride, the latter may be prevented from precipitating by adjusting the acidity of the solution.

3. Procedures have been given for the detection of small amounts of copper in the presence of relatively large quantities of foreign metals.

4. The reagent is more specific for copper than any of the other reagents heretofore proposed; and possesses an advantage over the ferrocyanide test in that small quantities of iron do not interfere with its use.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF FLUORIDES—THE ANALYSIS OF SILICATES AND CARBONATES FOR THEIR FERROUS IRON CONTENT.²

By O. L. BARNBRY.

Received February 15, 1915.

The permanganate titration of ferrous iron in the presence of chlorides has attracted attention for a considerable period of time because of the economic importance of the determination of iron, the ease with which iron ores dissolve in hydrochloric acid and the rapidity of conducting the permanganate titration. While the titration of iron with permanganate in hydrochloric acid solution has been studied by many inves-

¹ THIS JOURNAL, 35, 168 (1913).

² Read at the New Orleans Meeting of the American Chemical Society.

tigators,¹ the titration of iron in hydrofluoric acid solution has not received the attention which it merits, especially considering that this titration has been the source of much solicitude to the geologist, petrographer and chemist for many years. Hydrofluoric acid is the most efficient reagent known at present for the decomposition of a silicate. A permanganate solution is one of the most convenient oxidizing solutions available for oxidation. However, it is generally recognized that when ferrous iron is titrated with permanganate in hydrofluoric acid solution the end point is fleeting and the result high or worthless. Consequently any procedure which increases the accuracy of the titration of ferrous iron with permanganate in fluoride solution has direct application to a very important method of analysis. This study has for its object an improved determination of ferrous iron in fluoride solution and its application to the analysis of silicates and carbonates for their ferrous iron content.

Mitscherlich² proposed to decompose the mineral by heating with strong sulfuric acid in a closed tube for a considerable length of time, thus yielding ferrous sulfate, which was subsequently titrated with permanganate. Hillebrand and Stokes³ as well as de Koninck⁴ have shown that this method may give erroneous results in the presence of sulfides which cause the reduction of ferric to ferrous iron, which is later titrated, thus yielding a high percentage. Vogt⁵ mentions a similar reducing action of sulfides, Cu_2S being the specific reference.

J. P. Cooke, Jr.,⁶ first used sulfuric and hydrofluoric acids for the decomposition and analysis of silicates for their ferrous iron content. The method as proposed by him is in general use to-day. This method, in brief, consists in the decomposition of the silicate with sulfuric and hydrofluoric acids in an atmosphere free from oxygen and titration with permanganate. The air must be excluded to prevent the oxidation of the iron during solution. Cooke passed carbon dioxide through the so-called "Cooke water bath" with inverted funnel cover to exclude the air, added the acid, heated the water in the bath to boiling, shut off the flow of carbon dioxide, allowing the steam to keep the air away from the sample undergoing attack, waited until the silicate was thoroughly decomposed, then passed cold water through the bath to cool the solution, meanwhile passing carbon dioxide, diluted and then titrated the ferrous iron with permanganate.

¹ See Barnebey, *THIS JOURNAL*, 36, 1429 (1914).

² *J. prakt. Chem.*, 81, 108, 116 (1860); 83, 455 (1862).

³ *THIS JOURNAL*, 22, 625 (1900); *Z. anorg. Chem.*, 25, 326 (1900); Stokes, *Bull. U. S. Geol. Survey*, 186 (1901); *Am. J. Sci.*, [4] 12, 414 (1901).

⁴ *Ann. Soc. Geol. Belgique*, 10, 101 (1883); *Z. anorg. Chem.*, 26, 123 (1900).

⁵ *Z. prakt. geol.*, 1899, p. 250.

⁶ *Am. J. Sci.*, [2] 44, 347 (1867); see also Avery, *Chem. News*, 19, 270 (1869); Wilber and Whittlesey, *Ibid.*, 22, 2 (1870).

This method has several faults: (1), rigid care must be exercised to prevent partial oxidation of the dissolving ferrous iron during the decomposition period; (2), the end point may be more or less indefinite or fleeting; (3), certain naturally occurring substances must be absent or the results are vitiated.

Pratt¹ has attempted to obviate the first-mentioned difficulty by avoiding the use of the water bath and heating the platinum crucible containing the sulfuric and hydrofluoric acids directly, conducting carbon dioxide into the crucible by means of a platinum tube. By the direct heating process he was able to diminish the time of heating to about ten minutes. However, too great concentration of solution was found detrimental, as the strong, hot sulfuric acid had a tendency to oxidize ferrous sulfate. Hillebrand² obtained good results by this method.

Hillebrand² gives an excellent discussion of the detrimental influence of sulfides, vanadium and organic matter, stating that the titration is "entirely unreliable in the presence of organic matter." This author has also studied the effect of grinding upon the ferrous content of minerals, finding that fine pulverization decreases the quantity of ferrous iron found, which he attributes to the heat effect.

Gage³ seeks to improve the titration of the iron by the addition of calcium phosphate to precipitate the fluorine as calcium fluoride. Fromme⁴ adds a large amount of finely divided silicic acid, thus converting the hydrofluoric acid into fluosilicic acid. Dittrich⁵ used potassium sulfate with silicic acid to remove influence of the fluorine. Dittrich and Leonhard⁶ studied the use of the three previously mentioned reagents, recommending the use of 10 g. of finely divided silicic acid and 20-25 g. of potassium sulfate in a volume of 100 cc. which contained also 2 cc. of sulfuric acid. Deussen⁷ mentions that manganous sulfate, to a certain degree, does away with the source of error. However, this use of manganous sulfate has been shown to be not only of no value but of great detriment by several authors.⁸ Hillebrand⁸ states that

"It is possible to titrate ferrous iron in the presence of sulfuric acid, and as much as 5 to 7 cc. of 40% hydrofluoric acid in a total volume of 200 to 400 cc., almost if not quite as exactly as in sulfuric acid alone, provided the iron solution is diluted with air-free water and the titration made immediately after adding the hydrofluoric acid

¹ *Am. J. Sci.*, [3] **48**, 149 (1894).

² Hillebrand, "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Survey, *Bull.* **422** (1910).

³ *THIS JOURNAL*, **31**, 381 (1909).

⁴ *Tschermak's mineralog. u. petrogr. Mitteil.*, **28**, 329 (1909).

⁵ "3 Versammlung in Bad Dürkheim," am 29 März, 1910, II Teil, S 92-3; *Ber. Versam. Oberrhein. geol. Ver.*, **2**, 92; *Chem. Abst.*, **5**, 846 (1911).

⁶ *Z. anorg. Chem.*, **74**, 21 (1912).

⁷ *Ibid.*, **44**, 425 (1905).

⁸ Hillebrand, Gage, Dittrich and Leonhard, *Loc. cit.*

and with all possible dispatch." He says further, "in the presence of little ferrous iron, up to, say, 2 centigrams, and 5 to 7 cc. of 40% hydrofluoric acid the color produced by a drop of permanganate lasts some time, but is very evanescent as the ferrous iron, and consequently the manganese salt formed, increases."

In the following pages is outlined a systematic study of various types of agents which suggested themselves as interesting in regard to their effect on the titration of ferrous iron in the presence of fluorides. The effect of each agent is studied under varying conditions of concentration of that agent. Each series of experiments contains the results of a number of titrations with permanganate of measured volumes of standard ferrous sulfate in the presence of measured volumes of hydrofluoric acid and the agent being studied. The total volume in each case was 200 cc. preceding titration unless otherwise designated. Usually, after the end-point reading had been taken and recorded, 0.10 cc. of permanganate was added in excess, the solution then stirred and allowed to stand until the color bleached out. This procedure was adopted as a test on the stability of the end point. Ceresin beakers and hard rubber stirring rods were used.

TABLE I.—SULFURIC ACID AS PREVENTIVE.

1 cc. KMnO_4 = 0.009186 g. Fe.¹1 cc. FeSO_4 = 0.006151 g. Fe.²

| | Normality. | | Iron—Gram. | | Error. | Time 0.10 cc. KMnO_4 lasted. Seconds. |
|---------|---------------------------|-----|------------|--------------|---------|--|
| | H_2SO_4 . | HF. | Present. | Found. | | |
| 1..... | ... | 1.0 | 0.1538 | 0.1543 | +0.0005 | 10 |
| 2..... | 0.05 | 1.0 | 0.1538 | 0.1543 | +0.0005 | 10 |
| 3..... | 0.10 | 1.0 | 0.1538 | 0.1545 | +0.0007 | 15 |
| 4..... | 0.15 | 1.0 | 0.1538 | 0.1552 | +0.0014 | 25 |
| 5..... | 0.25 | 1.0 | 0.1538 | 0.1543 | +0.0005 | 40 |
| 6..... | 0.50 | 1.0 | 0.1538 | 0.1545 | +0.0007 | 70 |
| 7..... | 0.75 | 1.0 | 0.1538 | 0.1543 | +0.0005 | 120 |
| 8..... | 1.0 | 1.0 | 0.1538 | 0.1543 | +0.0005 | 140 |
| 9..... | 2.0 | 1.0 | 0.1538 | 0.1540 | +0.0002 | 130 |
| 10..... | 4.0 | 1.0 | 0.1538 | 0.1543 | +0.0005 | 120 |
| 11..... | 5.0 | 1.0 | 0.1538 | 0.1543 | +0.0005 | 120 |
| 12..... | 8.0 | 1.0 | 0.1538 | 0.1542 | +0.0004 | 30 |
| 13..... | 12.0 | 1.0 | 0.1538 | 0.1556 | +0.0018 | 3-4 |
| 14..... | 16.0 | 1.0 | 0.1538 | 0.16+ | | .. |
| 15..... | 1.0 | 1.5 | 0.1538 | 0.1545 | +0.0007 | 30 |
| 16..... | 1.0 | 2.5 | 0.1538 | 0.1550 | +0.0012 | 12 |
| 17..... | 1.0 | 5.0 | 0.1538 | No end point | | .. |
| 18..... | 5.0 | 5.0 | 0.1538 | No end point | | .. |

¹ The iron value of this and other permanganate solutions used in this investigation is the average value obtained by checking against sodium oxalate, ferrous ammonium sulfate and electrolytic iron.

² Approximately 240 g. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in water containing 20 cc. of conc. sulfuric acid (sp. gr. 1.84) and diluted to 8 l. This solution was titrated with the permanganate at the time of using and its value computed from the iron value of the permanganate.

Table I shows the effect of varying concentrations of sulfuric acid on this titration in presence of fluorides.

Experiments 6 to 11 inclusive show that ferrous iron can be titrated at room temperature with moderate accuracy in solutions normal in hydrofluoric acid and normal to 5 *N* sulfuric acid. However, considerably less, or more, sulfuric acid lessens the stability of the end point.

Titration in phosphoric acid solution of all concentrations between 0.1 *N* and 0.125 *N* with normal hydrofluoric acid present gives very fugitive end points. The use of solutions of the acid phosphates of the alkalis also gives very fleeting and indefinite end points. Hence phosphoric acid can not be substituted for sulfuric acid in this titration.

The influence of insoluble phosphates was tried to ascertain if they would give prevention of the indefiniteness of the fluoride end point. Phosphates of zinc, calcium,¹ magnesium, iron and aluminum were used. (See Table II.)

TABLE II.—PREVENTION BY PHOSPHATES INSOLUBLE IN WATER.

1 cc. $\text{KMnO}_4 = 0.005068$ g. Fe.

1 cc. $\text{FeSO}_4 = 0.005822$ g. Fe.

| | Normality. | | | Phosphate added. | Iron—Grams. | | | 0.10 cc. KMnO_4 lasted Seconds. |
|---------|---------------------------|---------------------------|---------------|--------------------------------|-------------|--------------|---------|--|
| | H_2SO_4 . | H_3PO_4 . | HF . | | Present. | Pound. | Error. | |
| 1..... | .. | .. | .0 | $\text{Ca}_3(\text{PO}_4)_2^3$ | 0.1456 | 0.1343 | —0.0113 | Fleeting |
| 2..... | .. | .. | .0 | $\text{Ca}_3(\text{PO}_4)_2^2$ | 0.1456 | 0.1368 | —0.0088 | Fleeting |
| 3..... | 0.75 | .. | .0 | $\text{Ca}_3(\text{PO}_4)_2^2$ | 0.1456 | 0.1456 | 0.0000 | Fleeting |
| 4..... | .. | .. | .0 | 5 g. " | 0.1456 | 0.1389 | —0.0067 | Fleeting |
| 5..... | .. | .. | .0 | 10 g. " | 0.1456 | 0.1363 | —0.0093 | Fleeting |
| 6..... | .. | .. | .0 | 20 g. " | 0.1456 | 0.1360 | —0.0096 | Fleeting |
| 7..... | .. | .. | .0 | 50 g. " | 0.1456 | 0.1302 | —0.0154 | Fleeting |
| 8..... | 0.60 | .. | .0 | 20 g. " | 0.1456 | 0.1457 | +0.0001 | 40 |
| 9..... | .. | 0.75 | .0 | 20 g. " | 0.1456 | 0.1409 | —0.0047 | Fleeting |
| 10..... | .. | 1.5 | .0 | 20 g. " | 0.1456 | 0.1429 | —0.0027 | Fleeting |
| 11..... | .. | 3.0 | .0 | 20 g. " | 0.1456 | 0.1455 | —0.0001 | Fleeting |
| 12..... | .. | .. | .0 | FePO_4^2 | 0.1456 | No end point | | Fleeting |
| 13..... | .. | .. | .0 | FePO_4^2 | 0.1456 | No end point | | Fleeting |
| 14..... | .. | .. | .0 | AlPO_4^2 | 0.1456 | 0.1461 | +0.0005 | 20 |
| 15..... | 0.50 | .. | .0 | AlPO_4^2 | 0.1456 | 0.1470 | +0.0014 | 20 |
| 16..... | .. | .. | .0 | $\text{Zn}_3(\text{PO}_4)_2^2$ | 0.1456 | 0.1464 | +0.0008 | 5 |
| 17..... | .. | .. | .0 | $\text{Zn}_3(\text{PO}_4)_2^2$ | 0.1456 | 0.1470 | +0.0014 | 5 |
| 18..... | .. | .. | .0 | $\text{Mg}_3(\text{PO}_4)_2^2$ | 0.1456 | 0.1368 | —0.0088 | 7 |
| 19..... | 0.50 | .. | .0 | $\text{Mg}_3(\text{PO}_4)_2^2$ | 0.1456 | 0.1414 | —0.0042 | 25 |
| 20..... | 0.50 | .. | .0 | $\text{Mg}_3(\text{PO}_4)_2^2$ | 0.1456 | 0.1427 | —0.0029 | 30 |
| 21..... | 1.0 | .. | .0 | $\text{Mg}_3(\text{PO}_4)_2^2$ | 0.1456 | 0.1449 | —0.0007 | 30 |
| 22..... | 2.0 | .. | .0 | $\text{Mg}_3(\text{PO}_4)_2^2$ | 0.1456 | 0.1455 | —0.0001 | .. |

Experiments 1, 2, 4, 5, 6, 7, 18, 19 and 20 gave low results because of precipitation of ferrous phosphate, which consequently was not completely

¹ Gage, *Loc. cit.*

² Added solid in excess.

oxidized by the permanganate. In 19 the phosphate was added before the sulfuric acid, in 20 the acid before the phosphate, which accounts for a higher result in 20. Experiments 8, 11 and 22 indicate that good results may be obtained when the proper adjustment is obtained between phosphate of calcium or magnesium and acid. However, with calcium phosphate and phosphoric acid the end points were fleeting and with magnesium phosphate and sulfuric acid the time test of 0.10 cc. of permanganate was not as favorable as when titrating in sulfuric acid solution without the phosphate (Table I). The results with calcium phosphate do not confirm the work of Gage. Ferric, aluminum and zinc phosphates gave poor results, those with the zinc salt being the best, but the end point was extremely fleeting. The phosphates tried seem to have little merit as preventives.

The action of alkali bisulfates is similar to the action of sulfuric acid, but the neutral alkali sulfates have but a slight tendency to prevent the fluoride influence.

The influence of a number of bivalent neutral sulfates was tried, among such being zinc, magnesium, calcium, mercury, cadmium and manganese sulfates. Zinc, cadmium and mercury sulfates give unstable end points which lack reliability. Calcium sulfate added as a solid in excess gives end points which are but slightly more stable. Magnesium sulfate is much more effective. (See Table III.)

TABLE III.—MAGNESIUM SULFATE AS PREVENTIVE.

1 cc. KMnO_4 = 0.009208 g. Fe.1 cc. FeSO_4 = 0.006151 g. Fe.

| Normal- ity. | HF. | 50% $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Cc. | Vol- ume. Cc. | Iron—Gram. | | | 0.10 cc. KMnO_4 lasts. |
|-----------------|-----|---|---------------------|------------|--------|---------|------------------------------------|
| | | | | Present. | Found. | Error. | |
| .0 | | 10 | 200 | 0.1538 | 0.1532 | —0.0006 | 30 sec. |
| .0 | | 20 | 200 | 0.1538 | 0.1535 | —0.0003 | 40 sec. |
| .0 | | 40 | 200 | 0.1538 | 0.1537 | —0.0001 | 110 sec. |
| .0 | | 80 | 200 | 0.1538 | 0.1539 | +0.0001 | 180 sec. |
| .0 | | 160 | 200 | 0.1538 | 0.1532 | —0.0006 | 20 min. |
| .8 | | 160 | 225 | 0.1538 | 0.1539 | +0.0001 | 4 min. |
| 7..... | 3.0 | 180 | 265 | 0.1538 | 0.1535 | —0.0003 | 90 sec. |
| 8..... | 3.0 | 210 | 335 | 0.1538 | 0.1548 | +0.0010 | 80 sec. |

When the hydrofluoric acid is added to a solution containing magnesium or vice versa, a very light precipitate forms. The amount of precipitate increases progressively with the concentration of the acid and magnesium. In Experiment 8 the precipitate was very heavy—probably fluoride of magnesium. The prevention of the fluorine influence is very marked, surprisingly so in view of the comparatively poor prevention of zinc sulfate.

The detrimental influence of manganese salts is shown in Table IV.

TABLE IV.—MANGANESE SULFATE AS PREVENTIVE.

 1 cc. $\text{KMnO}_4 = 0.007866 \text{ g. Fe.}$

 1 cc. $\text{FeSO}_4 = 0.006151 \text{ g. Fe.}$

 Manganese Solution I contains 80 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$, 150 cc. H_2SO_4 (sp. gr. 1.84) and 150 cc. H_3PO_4 (sp. gr. 1.7) per liter.

 Manganese Solution II = 500 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ per liter.

| | Normal- ity. HF. | Mn soln. I. Cc. | Mn soln. II. Cc. | Iron—Gram. | | | Remarks on end point. |
|--------|---------------------|--------------------|---|------------|--------------|---------|--------------------------|
| | | | | Present. | Found. | Error. | |
| 1..... | 1.0 | 1 | .. | 0.1538 | 0.1544 | +0.0006 | Fleeting |
| 2..... | 1.0 | 5 | .. | 0.1538 | 0.1544 | +0.0006 | Very fleeting |
| 3..... | 1.0 | 20 | .. | 0.1538 | No end point | | Very fleeting |
| 4..... | 1.0 | .. | 1 | 0.1538 | 0.1663 | +0.0125 | Very fleeting |
| 5..... | 1.0 | .. | 10 | 0.1538 | 0.17+ | | Very fleeting |
| 6..... | 1.0 | .. | 20 | 0.1538 | No end point | | Very fleeting |
| 7..... | 1.0 | .. | 40 | 0.1538 | No end point | | Very fleeting |
| 8..... | 1.0 | .. | 10 + 20 cc. of ion H_2SO_4 | 0.1538 | No end point | | Very fleeting |

Manganese salts are thus seen to vitiate results to an enormous extent; when present in any considerable quantity, they absolutely inhibit a good titration.

The effect of a number of trivalent sulfates was tried, and that of ferric sulfate found to be of most interest (Table V).

TABLE V.—FERRIC SULFATE AS PREVENTIVE.

 1 cc. $\text{KMnO}_4 = 0.009186 \text{ g. Fe.}$

 1 cc. $\text{FeSO}_4 = 0.006136 \text{ g. Fe.}$

$\text{Fe}_2(\text{SO}_4)_3$ Solution.—500 g. crystallized ferric sulfate + 40 cc. H_2SO_4 (sp. gr. 1.84) per liter.

| | Normal- ity. HF. | $\text{Fe}_2(\text{SO}_4)_3$ Cc. | Iron—Gram. | | | 10 cc. KMnO_4 lasted. |
|--------|---------------------|-------------------------------------|------------|--------|---------|-----------------------------------|
| | | | Present. | Found. | Error. | |
| 1..... | 1.0 | 10 | 0.1534 | 0.1531 | —0.0003 | 2 minutes |
| 2..... | 1.0 | 20 | 0.1534 | 0.1529 | —0.0005 | 5 minutes |
| 3..... | 1.0 | 40 | 0.1534 | 0.1529 | —0.0005 | 14 minutes |
| 4..... | 1.0 | 80 | 0.1534 | 0.1530 | —0.0004 | Time not taken. |
| 5..... | 3.0 | 200 | 0.1534 | 0.1516 | —0.0018 | (Volume, 325 cc.) |

Ferric sulfate gives good prevention, but with a large amount of hydrofluoric acid a light pink to lavender color is imparted to the solution which is somewhat troublesome (Experiments 4 and 5). When ferric sulfate is added to hydrofluoric acid solutions, the color of ferric salts disappears practically entirely until an excess of ferric iron has been added. Aluminum sulfate gave some preventive effect, but it was not sufficiently satisfactory to be of especial merit. A few experiments using bismuth sulfate were performed. While this salt seemed to improve the end point the improvement was not of sufficient degree to have any value for the purposes of this work. The effect of cerous sulfate was tried and found to be detrimental rather than beneficial.

Cobalt, chromium, nickel and copper sulfates gave colored solutions

when added to hydrofluoric acid solutions and thereby prevented the appearance of good end points.

The effect of a number of oxides was tried to ascertain if they react with the hydrofluoric acid so as to yield undissociated fluorides in solution. Oxides of aluminum, magnesium and zinc are not applicable inasmuch as when added in excess they precipitate hydroxide of iron, thus hindering a good clean-cut reaction. Addition of stannic oxide produced apparently no effect, giving a fleeting end point. The yellow color of tungstic oxide interfered during titration and the end point was not stable.

Table VI gives the tabulated results obtained using molybdic oxide.

TABLE VI.—MOLYBDIC OXIDE AS PREVENTIVE.

Iron and permanganate solutions the same as used in Series V.

| Normality. | | Solid MoO ₃ in excess. | Iron—Gram. | | | 10 cc. KMnO ₄ lasted. Seconds. |
|------------|------|--|------------|-----------------|-----------------|--|
| HF. | | | Present. | Found. | | |
| 1..... | 1.0 | | 0.1534 | 0.1536 <i>b</i> | 0.1542 <i>p</i> | 15 |
| 2..... | 2.0 | | 0.1534 | 0.1509 <i>b</i> | 0.1547 <i>p</i> | 6 |
| 3..... | 1.0 | | 0.1534 | 0.1538 <i>b</i> | 0.1540 <i>p</i> | 10 |
| 4..... | 1.0 | | 0.1534 | 0.1534 <i>b</i> | 0.1536 <i>p</i> | 16 |
| 5..... | 1.0 | | 0.0062 | 0.0073 <i>b</i> | 0.0073 <i>p</i> | * |
| 6..... | 1.0 | | 0.0006 | 0.0010 <i>b</i> | 0.0010 <i>p</i> | * |
| 7..... | 0.05 | | 0.0006 | 0.0010 <i>b</i> | 0.0010 <i>p</i> | * |
| 8..... | 1.0 | (NH ₄) ₂ MoO ₄ | 0.1534 | 0.1534 <i>b</i> | 0.1536 <i>p</i> | * |
| 9..... | 1.0 | solution | 0.1534 | 0.1532 <i>b</i> | 0.1534 <i>p</i> | * |

* Time not taken, but pink end point was fleeting in each case.

Results designated "b" were obtained by noting the volume of permanganate required to cause disappearance of the blue coloration formed by the reduction of the molybdenum by the ferrous iron. Results designated "p" are those obtained by utilizing the volume of permanganate required to tinge the solution pink.

Columbic and tantalic oxides apparently produced no effect because of the slow solution of these oxides in hydrofluoric acid. If freshly precipitated undoubtedly this action would be faster.

Titanium dioxide gives excellent prevention (Table VII).

TABLE VII.—TITANIUM DIOXIDE AS PREVENTIVE.

Iron and permanganate solutions the same as used in Series V.

| | Normality. HF. | Normality. H ₂ SO ₄ . | Solid TiO ₂ . | Iron—Gram. | | | 0.10 KMnO ₄ lasted. |
|--------|-------------------|--|-----------------------------|------------|--------|---------|-----------------------------------|
| | | | | Present. | Found. | Error. | |
| 1..... | 1.0 | .. | Excess | 0.1534 | 0.1539 | +0.0005 | 90 min. |
| 2..... | 2.0 | .. | Excess | 0.1534 | 0.1534 | 0.0000 | 60 min. |
| 3..... | 5.0 | .. | Excess | 0.1534 | 0.1533 | -0.0001 | 25 min. |
| 4..... | 1.0 | 1.0 | Excess | 0.1534 | 0.1534 | 0.0000 | 80 min. |

Silica and silicic acid were used as preventives. The silicic acid was made in the solution by adding sodium silicate to the acid solution containing ferrous iron and hydrofluoric acid (Table VIII).

TABLE VIII.—SILICIC ACID AS PREVENTIVE.

 1 cc. KMnO_4 = 0.007814 g. Fe.

 1 cc. FeSO_4 = 0.006151 g. Fe.

 Na_2SiO_3 —

| | Normal- ity. HF. | Normality. H_2SO_4 . | Cc. Na_2SiO_3 . | Iron—Gram. | | | 0.10 cc. lasted. |
|--------|---------------------|---|------------------------------------|------------|--------|---------|---------------------|
| | | | | Present. | Found. | Error. | |
| 1..... | 1.0 | 0.5 | 10 | 0.1230 | 0.1230 | 0.0000 | 80 seconds |
| 2..... | 2.0 | 1.0 | 25 | 0.1230 | 0.1180 | —0.0050 | 40 seconds |
| 3..... | 2.0 | 2.0 | 20 | 0.1230 | 0.1225 | —0.0005 | 60 seconds |
| 4..... | 2.0 | 2.0 | .. | 0.1230 | 0.1250 | +0.0020 | 20 seconds |
| 5..... | 5.0 | 2.0 | .. | 0.1230 | 0.1266 | +0.0036 | Very unstable |
| 6..... | 5.0 | 2.0 | 25 | 0.1230 | 0.1238 | +0.0008 | 60 seconds |

Experiments 1, 3 and 6 show that moderately good results can be obtained by using silicic acid as preventive. In Experiment 2 too much silicate was added in proportion to the amount of acid present and some of the ferrous iron was precipitated, hence the low result. Experiments 4 and 5 are included to show the relative values obtained in presence of hydrofluoric acid with sulfuric acid compared with sulfuric acid plus the silicic acid.

Granulated silica, prepared by various chemical manufacturers was tried but it did not work so well. The pink end point of the permanganate was far less stable, giving a tendency toward high results, perhaps owing to the more insoluble nature of the silica, or to slight impurities in the silica, or to both causes.

When boric acid is added to hydrofluoric acid in solution, meta-fluoboric acid, HBF_4 , is formed, which does not dissociate appreciably to yield hydrofluoric acid in the presence of boric acid. This is illustrated by the fact that a dilute solution of the same will not attack glass.¹

Table IX gives the results of a study of the effect of boric acid in removing the influence of the fluorine when titrating ferrous salts.

TABLE IX.—BORIC ACID AS PREVENTIVE.

 1 cc. KMnO_4 = 0.007866 g. Fe.

 1 cc. FeSO_4 = 0.006156 g. Fe.

| | Normal- ity. HF. | Normality. H_2SO_4 . | H_2BO_3 solid. | Iron—Gram. | | | 10 cc. KMnO_4 lasted. |
|--------|---------------------|---|-----------------------------------|------------|--------|---------|-----------------------------------|
| | | | | Present. | Found. | Error. | |
| 1..... | 0.50 | .. | Excess | 0.1231 | 0.1234 | —0.0003 | 40 min. |
| 2..... | 1.0 | .. | Excess | 0.1231 | 0.1232 | +0.0001 | 40 min. |
| 3..... | 2.0 | .. | Excess | 0.1231 | 0.1232 | +0.0001 | 20 min. |
| 4..... | 5.0 | .. | Excess | 0.1231 | 0.1230 | —0.0001 | 10 min. |
| 5..... | 1.0 | 0.50 | Excess | 0.1231 | 0.1232 | +0.0001 | 15 min. |
| 6..... | 0.50 | .. | Excess | 0.2462 | 0.2460 | —0.0002 | 80 min. |

The six experiments of Table IX indicate a very high degree of efficiency for the boric acid. In Experiment 4 considerable heat was evolved when the boric acid was added. The amount of solid added in each case

¹ See also Moissan, *Traite de Chimie Minerale*, 2, 166 (1904).

depended upon the consumption of the boric acid by the hydrofluoric acid. This is easily regulated, since an excess of reagent does no harm. In fact the excess seems to facilitate obtaining the end point.

Borax was also tried, adding the solid in excess to the sulfate solution containing HF. Its use produced good end points, but not as excellent as with boric acid. A saturated solution of borax was also used with success. Inasmuch as the use of boric acid affords such good titrations a point of interest arises at once in regard to how much effect it will have in offsetting the detrimental influence of manganese salts. This is of especial importance, inasmuch as manganese salts have such a good preventive action when titrating ferrous iron in the presence of chlorides and bromides (Table X).

TABLE X.—BORIC ACID PREVENTION OF THE MANGANESE EFFECT.

Solutions of iron and permanganate the same as in Series IV.

| | Normal- ity. HF. | Normal- ity. HCl. | Mn soln. | | Boric acid. | Iron—Gram. | | 0.10 cc. KMnO_4 lasted. |
|--------|------------------------|-------------------------|-----------|------------|-----------------|------------|--------|----------------------------------|
| | | | I. Cc. | II. Cc. | | Present. | Found. | |
| 1.... | 1.0 | .. | 1 | .. | Solid in excess | 0.1538 | 0.1538 | Definite; time not noted. |
| 2.... | 1.0 | .. | 5 | .. | Solid in excess | 0.1538 | 0.1533 | Definite; time not noted. |
| 3.... | 1.0 | .. | 20 | .. | Solid in excess | 0.1538 | 0.1539 | Definite; time not noted. |
| 4.... | 1.0 | 0.03 | 20 | .. | Solid in excess | 0.1538 | 0.1536 | 60 seconds |
| 5.... | 1.0 | 0.15 | 20 | .. | Solid in excess | 0.1538 | 0.1538 | 40 seconds |
| 6.... | 1.0 | 0.30 | 20 | .. | Solid in excess | 0.1538 | 0.1538 | 35 seconds |
| 7.... | 1.0 | 0.60 | 20 | .. | Solid in excess | 0.1538 | 0.1542 | 20 seconds |
| 8.... | 1.0 | 0.90 | 20 | .. | Solid in excess | 0.1538 | 0.1536 | 12 seconds |
| 9.... | 1.0 | 0.90 | 30 | .. | Solid in excess | 0.1538 | 0.1538 | 20 seconds |
| 10.... | 1.0 | 1.5 | 50 | .. | Solid in excess | 0.1538 | 0.1551 | 20 seconds |
| 11.... | .. | 0.60 | .. | .. | Solid in excess | 0.1538 | 0.1571 | Not definite. |
| 12.... | 1.0 | .. | .. | 10 | Solid in excess | 0.1538 | 0.1533 | 40 seconds |
| 13.... | 1.0 | .. | .. | 40 | Solid in excess | 0.1538 | 0.1543 | 5 seconds |
| 14.... | 1.0 | 0.60 | .. | 10 | Solid in excess | 0.1538 | 0.1539 | 4 seconds |
| 15.... | 1.0 | .. | .. | .. | Solid in excess | 0.1538 | 0.1538 | 120 seconds |

In the experiments of Table X the time listed for disappearance of the pink color of the permanganate is only for the disappearance of the deep pink; a lighter shade of pink remained (except in Expts. 11, 13, 14) for a longer period of time than that designated. In Expt. 11 the odor of liberated chlorine was strong. In Expt. 15 after the 0.10 cc. of KMnO_4 added in excess had bleached, 0.10 cc. more of KMnO_4 was added and this addition required 18 minutes to bleach, after which 0.10 cc. more of KMnO_4 retained its pink color for over three hours. This series of experiments shows that the fluorine influence can be removed in the presence of manganous salts very effectively. Hence, in the presence of fluorides, bromides and chlorides the addition of a manganese salt and boric acid allows ferrous iron to be titrated accurately with permanganate.

Inasmuch as hydrofluoric acid solutions of ferrous iron are readily

oxidized by the air, it was decided to study the stability of fluoboric acid solutions of ferrous iron. To measured portions of standard ferrous sulfate were added measured volumes of 10 *N* HF; the solutions were diluted to a definite volume and allowed to stand varying lengths of time after which boric acid was added in excess and the ferrous iron titrated. These results were compared with those obtained by adding an excess of boric acid to the fluoride solution immediately after adding the hydrofluoric acid and allowing to stand an equal time.

TABLE XI.—STABILITY OF FLUOBORIC ACID SOLUTIONS OF FERROUS IRON.

| | | | | | | | | | | | | | |
|------|------|------------|----|--------------|--------|---|--|----------|--|---|--|----------|--|
| | | | | | | | | | | 1 cc. FeSO_4 = 0.006113 g. Fe. | | | |
| | | | | | | | | | | 1 cc. KMnO_4 = 0.009184 g. Fe. | | | |
| | | Normality. | | | | Iron—Gram. | | | | | | | |
| | | HF. | | Vol- ume. | | Time. | | Present. | | Found. | | Remarks. | |
| 1.. | 1.33 | 150 | 10 | 0.0611 | 0.0551 | Solid boric acid added after standing. | | | | | | | |
| 2.. | 1.33 | 150 | 20 | 0.0611 | 0.0543 | Solid boric acid added after standing. | | | | | | | |
| 3.. | 1.33 | 150 | 40 | 0.0611 | 0.0518 | Solid boric acid added after standing. | | | | | | | |
| 4.. | 1.33 | 150 | 30 | 0.1223 | 0.1139 | Solid boric acid added after standing. | | | | | | | |
| 5.. | 1.33 | 150 | 30 | 0.3057 | 0.2948 | Solid boric acid added after standing. | | | | | | | |
| 6.. | 1.33 | 150 | 10 | 0.0611 | 0.0613 | Solid boric acid added in excess before standing. | | | | | | | |
| 7.. | 1.33 | 150 | 20 | 0.0611 | 0.0611 | Solid boric acid added in excess before standing. | | | | | | | |
| 8.. | 1.33 | 150 | 40 | 0.0611 | 0.0613 | Solid boric acid added in excess before standing. | | | | | | | |
| 9.. | 1.33 | 150 | 30 | 0.1223 | 0.1223 | Solid boric acid added in excess before standing. | | | | | | | |
| 10.. | 1.33 | 150 | 30 | 0.3057 | 0.3053 | Solid boric acid added in excess before standing. | | | | | | | |
| 11.. | 1.33 | 100 | 60 | 0.1834 | 0.0743 | No boric acid added. Aerated. | | | | | | | |
| 12.. | 1.33 | 100 | 60 | 0.1834 | 0.1834 | Solid boric acid added in excess. Aerated. | | | | | | | |

Analysis of Silicate and Carbonate Rocks.

An appropriate sample (0.5 to 5 g.) in a capacious platinum dish is covered with water and placed on a Cooke water bath¹ in which the water has been previously thoroughly boiled to remove dissolved oxygen. Carbon dioxide is passed for several minutes, or steam allowed to escape for several minutes, or both, to remove any air inside of the glass funnel, after which 5 cc. of 1:1 H_2SO_4 (HCl can be used) is added by pouring down the platinum stirring rod. If carbonates are present care must be exercised to prevent too violent action. Should soluble sulfides be present the acid is likewise added slowly to expel the H_2S as completely as possible. Strong hydrofluoric acid is then added, 5 cc. to 20 cc. depending upon the size of the sample, pouring down the stirring rod. The bath is maintained at an even temperature, a continuous current of steam being expelled through the funnel until the silicate is thoroughly decomposed. If carbon dioxide is allowed to pass through the bath continuously it should be regulated so that its passage is slow, just sufficient to give direction to the current of escaping gases. Occasionally a little previously boiled water is added to the bath to maintain the water level. For this purpose a flask of boiling water should be kept constantly ready for use.

When decomposition is complete the funnel is lifted from its place and cold (previously boiled) distilled water added immediately to the dish to dilute the solution somewhat, followed immediately by an excess of solid boric acid. The solution is stirred, then lifted from the bath. If solid organic matter is present it should be filtered through an asbestos filter using suction (a carbon funnel with a Witte plate is convenient for this purpose) and the filter washed with previously boiled distilled water. The solution is poured into a glass beaker, diluted to a convenient volume, and titrated with standard permanganate. If the solution has been filtered it is titrated in the suction flask. It is well to add some solid boric acid before titrating to give the same color effect as usual at the end point. When hydrochloric acid is used for the decomposition of the sample, some substance should be added to counteract its influence when the ferrous iron is titrated. Since the hydrofluoric acid has been transposed to fluoboric acid any good preventive¹ is applicable. Ten to twenty cc. of the ordinary preventive solution² used in the iron titration (80 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ + 80 cc. H_2SO_4 (sp. gr. 1.84) + 80 cc. H_3PO_4 (sp. gr. 1.7) per liter is effective, or the phosphoric acid may be omitted and 160 cc. of sulfuric acid used instead in preparing this solution.

The above method can be easily adapted to Pratt's³ scheme of decomposing the silicate, which requires less time because of the application

¹ Cooke, *Loc. cit.*

² Barnebey, *Ibid.*

³ Pratt, *Ibid.*

of a higher temperature. The sample is placed in a platinum crucible, carbon dioxide is conducted into the crucible by means of a platinum tube, which is inserted under one edge of the cover, acid is added and heat applied directly to the crucible. As soon as steam is evolved copiously the carbon dioxide is shut off, hydrofluoric acid added and the cover fitted snugly to the crucible. When decomposition is complete dilute somewhat with water, add boric acid and proceed as usual.

Notes on the Method.

1. Scrupulous care must be exercised to exclude the air when decomposing the silicate with hydrofluoric acid in order to prevent oxidation. However, after the addition of the boric acid the ferrous solution becomes quite stable.

2. A carbon dioxide generator, after filling with carbonate (marble) and acid, should be allowed to generate carbon dioxide for a considerable period of time to remove the air as completely as possible. (Heating magnesite would probably be a still better method for obtaining carbon dioxide.) Only recently boiled water should be used in the water bath and only recently boiled distilled water added to the sample.

3. Until accustomed to the method of analysis the analyst should always check his procedure by heating measured volumes of standard ferrous iron solution with hydrofluoric acid, and titrating with the same manipulation as in the analysis in order to ascertain if the air is being excluded effectively.

4. Filtration is desirable when solid organic matter is visible after the sample is thoroughly decomposed. Filtration may not remove all the influence of the organic matter, however. The soluble organic matter naturally still has opportunity to give a reducing effect. If the clear solution is slightly colored by the presence of organic matter it should be largely diluted and titrated to the first distinct pink tinge of the solution. The presence of organic matter makes the end point much less stable than in its absence. Another procedure can be substituted for filtration. The sample can be transferred to a volumetric flask, diluted to the mark and the residue allowed to settle, after which portions can be withdrawn with a pipette and titrated.

5. Instead of adding solid boric acid the fluoride solution can be poured directly into an excess of a saturated solution of boric acid.

6. A convenient strength of permanganate for titrating samples low in ferrous iron content is 1 cc. = 0.001 g. FeO .

Samples 1-5, inclusive (Table XII), contained no organic matter and were free from sulfides. The end points were fleeting in analyses 2a, 3a and 4a, especially the last two. Samples 6-8, inclusive, contained considerable organic matter. In analysis 6a the result is only approximate,

as the end point was very fugitive because of the organic matter present. In 6b, 6c, 6d, 6e the solutions were filtered, as also were the samples 7b and 7c as well as 8b and 8c. Larger portions could have been used to advantage in Samples 5, 7 and 8. Samples were not analyzed according to procedure "a" for 7 and 8 because of the presence of large amounts of organic matter. Naturally filtration of the hydrofluoric acid solution is not advisable on account of the rapidity of oxidation of ferrous iron in such a solution by the air and also because of the action of the solution on glass.

TABLE XII.—ANALYSES OF SILICATES FOR FERROUS IRON.

1 cc. KMnO_4 = 0.001 g. FeO .

| Number. | Sample. Grams. | Per cent. FeO . | | | | |
|---------|-------------------|--------------------------|-------|----------------|-------|-------|
| | | a. | b. | c. | d. | e. |
| 1..... | 4.0 | 0.12 | 0.08 | 0.10 | ... | 0.08 |
| 2..... | 2.0 | 3.74 | 3.54 | 3.48 | 3.56 | 3.45 |
| 3..... | 1.0 | 6.94 | 6.49 | 6.45 | ... | 6.50 |
| 4..... | 0.4 | 14.70 | 14.36 | 14.36 14.48 | ... | 14.42 |
| 5..... | 2.0 | 0.09 | 0.084 | 0.085 | 0.078 | 0.080 |
| 6..... | 1.0 | 6.20 | 5.47 | 5.26 5.46 | 5.46 | 5.48 |
| 7..... | 2.5 | | 0.51 | 0.51 | ... | |
| 8..... | 1.0 | | 0.43 | 0.45 | ... | |

a. Sulfuric and hydrofluoric acids used for decomposition. No boric acid was added.

b. Decomposed like a. Boric acid was added.

c. Hydrofluoric acid used for decomposition. Boric acid was added.

d. Decomposed with hydrochloric and hydrofluoric acids. Manganese sulfate (80 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ per liter) and boric acid were added.

e. Decomposed like d. Manganese solution I and boric acid were added.

The results obtained by decomposition methods "b," "c," "d" and "e" are somewhat lower than those obtained by "a," but they are believed to be more accurate. The author prefers the use of sulfuric acid with hydrofluoric acid for decomposition of a silicate whenever this method of attack is applicable, although hydrochloric acid with hydrofluoric acid or hydrofluoric acid alone can be used satisfactorily. The chlorine influence on the titration must always be removed when hydrochloric acid is utilized.

Naturally, when the above method is applied to the analysis of carbonate rocks, the addition of hydrofluoric acid may be omitted if the sample is thoroughly decomposed by the other acids, or if only the iron existing as carbonate is desired. However, the hydrofluoric acid finds application if considerable siliceous matter is present and the total ferrous iron content of the sample is wanted.

The action of these preventives may be classified as follows: Class (a)

removes most, if not all, of the active hydrofluoric acid by the presence of another acid through the medium of which the oxidation proceeds by virtue of its greater strength as an acid or by mass action. Sulfuric acid by conductivity measurements is stronger than hydrofluoric acid; phosphoric acid is much weaker. Hence sulfuric acid gives fairly good and phosphoric acid poor prevention. The acid salts found to be of worth are valuable mostly for their acidity, *i. e.*, NaHSO_4 , KHSO_4 . (b) Certain salts react with the fluorides present, forming undissociated fluorides and salts of other acids than hydrofluoric, through the medium of which the reaction proceeds. Examples of this class of preventives are ferric and magnesium sulfates. Phosphates are not desirable inasmuch as they yield phosphoric acid by interaction with hydrofluoric acid, and phosphoric acid is to be avoided in the titration unless all the hydrofluoric acid is removed. Of the neutral phosphates only those of the alkalis are soluble in water, hence to add metal phosphates either the solids or the phosphate dissolved in phosphoric acid must be added, thus forming acid phosphates in most instances and again bringing the phosphoric acid into predominance. Still another difficulty arises from the use of phosphates; sufficient acidity must be present to prevent ferrous phosphate from precipitating. If the ratio of phosphate to acid does not give sufficient acidity the titration is worthless, being low. Classes (a) and (b) are so closely related that they could properly be included in one class, but in (a) hydrofluoric acid is present and in (b) a fluoride. (c) Other reagents react with hydrofluoric acid in such a manner as to combine the fluorine in the anion which does not dissociate to yield hydrofluoric acid. Boric and silicic acid are such preventives, forming fluoboric and fluosilicic acids by interaction with hydrofluoric acid.

Of the preventives tried the author prefers boric acid. This acid can be obtained on the market in a high degree of purity and is a cheap commodity. It gives a solution which is clear. The solubility of boric acid in water peculiarly fits it for this purpose, being sufficiently high to allow a rapid reaction with hydrofluoric acid and yet not so high as to cause waste of the chemical when adding the solid in slight excess. The appearance of solid boric acid in excess likewise indicates that sufficient reagent has been added to react with the hydrofluoric acid present. This is a distinct advantage when titrating solutions containing unknown or variable quantities of hydrofluoric acid. Solid boric acid in excess is advantageous rather than detrimental in obtaining the end point. The fluoboric acid solution of ferrous iron oxidizes very slowly in the air, thus removing an undesirable feature of the titration accompanying the usual methods for determining ferrous iron. It gives the best prevention of the hydrofluoric influence during titration.

Summary.

1. This study confirms earlier work which has shown that the permanganate titration of ferrous iron in the presence of fluorides gives an unstable end point, the instability increasing with increased concentrations of iron and hydrofluoric acid.

2. The use of sulfuric acid of normal to 5 *N* concentrations permits a good titration to be made in the presence of normal hydrofluoric acid. Phosphoric acid can not be substituted for sulfuric acid, since the former yields a fugitive end point. Certain acid sulfates accomplish the same result as the free acid.

3. Certain sulfates, *i. e.*, ferric and magnesium sulfates, react with the hydrofluoric acid and check its influence in the titration. Phosphates and acid phosphates are undesirable for prevention of the fluoride influence.

4. Certain oxides also have prevention tendencies, *i. e.*, molybdenum trioxide and titanium dioxide, the titanium dioxide being the better. The hydrofluoric acid may combine with the titanium and molybdenum, forming simple fluorides or fluotitanic and fluomolybdic acids. Boric acid and silicic acid remove the hydrofluoric acid, forming fluoboric and fluosilicic acids. Boric acid is the most effective of all reagents studied.

5. Ferrous iron solutions containing fluoboric acid are quite stable in the presence of air.

6. The prevention of the reagents studied may be classified in three divisions: (1) addition of a stronger acid than hydrofluoric acid for the solution medium, (2) conversion to salts of other acids forming also undissociated or sparingly dissociated fluorides by mass action of the preventer, and (3) conversion of the hydrofluoric acid to a complex acid which when dissociated, gives a complex anion rather than the simple fluorine ion.

7. A modified procedure is given for the analysis of silicate or carbonate rocks for their ferrous iron content, using boric acid to remove the detrimental influence of the hydrofluoric acid.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

THE PERMANGANATE AND IODIMETRIC DETERMINATION OF IODIDE IN PRESENCE OF CHLORIDE AND BROMIDE.¹

BY O. L. BARNEBEY.

Received February 15, 1915.

The permanganate oxidation of iodide to iodate originated with Pean de Saint Gilles.² A large number of modifications of this method have

¹ Read at the New Orleans meeting of the American Chemical Society.

² Pean de Saint Gilles, *Compt. rend.*, 46, 624 (1858).

been made but they still retain the fundamental idea of conversion of iodide to iodate. Certain authors use other oxidizing agents, such as nickelic oxide,¹ potassium dichromate,² chlorine³ to accomplish the same purpose.

Theoretically this reaction has many points in its favor, the essential one being its application to the estimation of small quantities of iodides. For this purpose the addition of three oxygen atoms to the iodide demands a sufficiently large quantity of oxidizing agent to make the titration quite accurate. The measure of the amount of oxidizing agent required or of the iodate formed gives two means for the quantitative determination of iodides.

Pean de Saint Gilles⁴ determined the quantity of iodide by adding an excess of permanganate to the neutral or alkaline solution, heating a few minutes, adding an excess of ferrous sulfate containing sulfuric acid and then titrating the excess of ferrous iron remaining in the solution. Hence the original method consists of a measure of the oxidation of iodide to iodate from the quantity of permanganate required. Klemp⁵ adds zinc chloride to facilitate precipitation of the manganese and watches for the appearance of the permanganate color in the supernatant liquid. The end point is obscure, however, and continuous heating and cautious addition of permanganate is required to obtain even a moderately good result. Reinige⁶ determined the excess of permanganate with sodium thiosulfate. Sonstadt⁷ precipitates the iodic acid formed by this reaction with barium chloride, transforms the barium iodate with potassium sulfate to potassium iodate and then estimates the amount of iodate "either gravimetrically or iodimetrically." Other investigators have destroyed the excess of permanganate with such agents as alcohol⁸ or hydrogen peroxide,⁹ filtered out the hydrated manganese dioxide and then titrated the iodic acid in the filtrate iodimetrically. Sodium sulfite¹⁰ has been used to reduce the permanganate, later reducing iodic to hydriodic acid and converting to silver iodide. McCullock¹¹ pointed out that the measure

¹ McCullock, *Chem. News*, 57, 45 (1888).

² Baubigny and Chavanne, *Compt. rend.*, 136, 1197 (1903); *Chem. Ztg.*, 28, 555 (1903); Emde, *Ibid.*, 35, 450 (1911).

³ Hunter, *J. Biol. Chem.*, 7, 321 (1910); *Proc. Soc. Exp. Biol. Med.*, 7, 10 (1910); Kendall, *THIS JOURNAL*, 34, 894 (1912).

⁴ Pean de Saint Gilles, *Compt. rend.*, 46, 624 (1858).

⁵ Klemp, *Z. anal. Chem.*, 20, 248 (1881).

⁶ Reinige, *Ibid.*, 9, 39 (1870).

⁷ Sonstadt, *Chem. News*, 26, 173 (1872).

⁸ Gröger, *Z. angew. Chem.*, 7, 52 (1894); Longi and Bonavia, *Gazz. chim. ital.*, 28, 325 (1898); Bernier and Peron, *J. pharm. chim.*, 3, 242 (1911); 4, 151 (1911); Knudsen, *Chem. Eng.*, 17, 119 (1913).

⁹ Auger, *Bull. soc. chim.*, 11, 615 (1912).

¹⁰ Baubigny and Rivals, *Compt. rend.*, 137, 927 (1903).

¹¹ McCullock, *Chem. News*, 57, 45, 135 (1888). McCullock also titrates iodide in presence of cyanide in sulfuric acid solution with permanganate, converting the iodide to iodine cyanide. In presence of strong hydrochloric acid titration yields ICI; hydrobromic acid yields BrI.

of the available oxygen from the hydrated manganese precipitate gives erroneous results, inasmuch as the precipitate is not pure manganese dioxide, but contains some manganous manganese. This condition of mixed oxides is one that might be anticipated from the general chemistry of the oxides of manganese. The oxide precipitated by the interaction of a reducing agent on permanganate or manganate or by an oxidizing agent on manganous manganese almost, if not invariably, contains part of its manganese in a lower state of oxidation than four.¹ The titration of iodic acid iodimetrically with thiosulfate, after removal of the excess of permanganate by alcohol or similar reducing agent and subsequent removal of the resulting manganese dioxide by filtration, removes the difficulty of an inconstant manganese oxide product of reaction and lessens filtration troubles, inasmuch as a considerable excess of permanganate can be employed and heating continued, if necessary, until the solution is quite easily filtered. The use of hydrogen peroxide² or alkali sulfites³ for the removal of the excess of permanganate would necessitate great care to avoid reduction of an appreciable amount of iodate, as these reducing agents are used to effect quantitative reduction of iodate to iodide.

Investigators using chlorine or hypochlorite have removed the excess of oxidizing agent by means of a current of air,⁴ boiling,⁵ or phenol.⁶ However, the general idea remains the same, conversion of the iodide to iodate and ascertaining the quantity of iodate formed.

The investigation to be outlined in the following pages is divided into two parts: (1) the permanganate titration according to the original and modified method of Pean de Saint Gilles and (2) the iodimetric titration of the iodate formed by the permanganate oxidation of the iodide.

1. The Permanganate Titration of Iodides.

The success or failure of the permanganate method as outlined by Pean de St. Gilles is dependent for the most part on the quantitative oxidation of ferrous to ferric iron by the permanganate in the presence of chloride and bromide. When the titration of ferrous iron with permanganate is attempted in the presence of halides in acid solution free halogen is liberated, the ease with which this liberation occurs increasing in the order hydrochloric, hydrobromic and hydriodic acids. The effect of chlorides

¹ J. Volhard, *Ann. Chem. Pharm.*, **198**, 318 (1879); Meineke, *Rep. d. anal. Chem.*, **3**, 337 (1883); **5**, 1 (1885); Hintz, *Z. anal. Chem.*, **24**, 421 (1885); Weber, *Ibid.*, **43**, 564, 643 (1904).

² Lenssen, *J. prakt. Chem.*, **81**, 276 (1860); Jannasch and Aschoff, *Z. anorg. Chem.*, **1**, 144, 245 (1892); **5**, 8 (1894).

³ Emde, *Chem. Ztg.*, **35**, 450 (1911).

⁴ Gil, *Rev. real. acad. cien.*, Madrid, **8**, 272; *Chem. Abst.*, **4**, 2616 (1910).

⁵ Hunter, *Loc. cit.*

⁶ Kendall, *Ibid.*

has been studied by a number of investigators¹ and various reagents have been used to prevent the detrimental influence of chlorides. Manganous salts have been found to be particularly effective. The author finds that manganous salts² also prevent the evolution of bromine, the best results being obtained in phosphoric acid solution.

If an alkaline solution containing chloride or bromide and permanganate is treated with ferrous sulfate acidified with sulfuric acid, chlorine (or hypochlorous acid) or bromine is liberated. If the acid ferrous sulfate solution is added in sufficient quantity all at once, thus insuring acidity only when the iron solution can give reduction at the same instant as acidity, then the liberation of halogen is greatly diminished. However, if sufficient manganous sulfate is added to the ferrous sulfate solution, which contains phosphoric acid, before the ferrous iron solution is added to the permanganate solution, then the tendency toward halogen liberation can be completely eliminated. The ferrous iron in the resulting solution can then be titrated accurately with permanganate.

Several series of analyses, in which the time of heating the iodide with permanganate was studied, showed that the heating should be continued a few minutes after the solution reached boiling temperature. Five minutes sufficed in every case. The effect of varying alkalinity was also tried and a low concentration of alkali found to give the best results. In acid solutions free iodine is liberated, which is transposed to iodic acid in part. If the concentration of acid is low, some iodine is liberated, complete conversion to free iodine being effected when the acid attains sufficient strength. In neutral solution the transposition is complete to iodic acid, but more time is required than in alkaline solution. Inasmuch as strong alkaline solutions of permanganate on heating decompose to a greater or less extent, liberating oxygen, a 0.01 *N* solution of sodium hydroxide was chosen for this work, 1 cc. of normal alkali being added for each 100 cc. of solution present. Heating just below boiling for five minutes a 0.01 *N* sodium hydroxide solution containing a moderate amount of permanganate (10–20 cc. of 0.1 *N* solution) causes a loss of oxygen which is so small as to be negligible. In fact such solutions give very little loss when heated for sixty minutes.

When a considerable quantity of iodic acid is treated with a large excess of ferrous iron in acid solution more or less reduction of the iodate occurs, simultaneously oxidizing the iron and liberating free iodine. To ascertain the extent of the reducing effect of ferrous iron on iodic acid in the presence of varying concentrations of sulfuric and phosphoric acids, a series of experiments was performed (Table I). In this series the quantity of potassium iodate was kept constant throughout and the other

¹ See Barnebey, *THIS JOURNAL*, 36, 1429 (1914).

² See also Phelps, *Am. J. Sci.*, 17, 201 (1904).

factors varied in a systematic manner. Each experiment was performed at room temperature. Each solution was allowed to stand 5 minutes after mixing the reagents. The volume before titration was 200 cc. in each case.

TABLE I.—REDUCTION OF IODIC ACID BY FERROUS SULFATE.

1 cc. KMnO_4 = 0.009208 g. Fe.

1 cc. FeSO_4 = 0.658 cc. KMnO_4 .

50 cc. of 0.1 N KIO_3 (3.5678 g. per liter) used in each experiment.

| Normality. | | Iron—Gram. | | | Normality. | | Iron—Gram. | | |
|---------------------------|--|------------|--------|---------|---------------------------|--|------------|--------|---------|
| H_2SO_4 . | H_3PO_4 . ¹ | Present. | Found. | Error. | H_2SO_4 . | H_3PO_4 . ¹ | Present. | Found. | Error. |
| 0.5 | ... | 0.0606 | 0.0608 | +0.0002 | ... | 1.0 | 0.0606 | 0.0610 | +0.0004 |
| 0.5 | ... | 0.1212 | 0.1213 | +0.0001 | ... | 1.0 | 0.1212 | 0.1212 | 0.0000 |
| 0.5 | ... | 0.1818 | 0.1818 | 0.0000 | ... | 1.0 | 0.1818 | 0.1812 | -0.0006 |
| 0.5 | ... | 0.2424 | 0.2422 | -0.0002 | ... | 1.0 | 0.2424 | 0.2410 | -0.0014 |
| 0.5 | ... | 0.3030 | 0.3029 | -0.0001 | ... | 1.0 | 0.3030 | 0.3011 | -0.0019 |
| ... | 0.5 | 0.0606 | 0.0606 | 0.0000 | 1.5 | ... | 0.0606 | 0.0608 | +0.0002 |
| ... | 0.5 | 0.1212 | 0.1213 | +0.0001 | 1.5 | ... | 0.1212 | 0.1208 | -0.0004 |
| ... | 0.5 | 0.1818 | 0.1818 | 0.0000 | 1.5 | ... | 0.1818 | 0.1812 | -0.0006 |
| ... | 0.5 | 0.2424 | 0.2420 | -0.0004 | ... | 1.5 | 0.0606 | 0.0608 | +0.0002 |
| ... | 0.5 | 0.3030 | 0.3029 | -0.0001 | ... | 1.5 | 0.1212 | 0.1210 | -0.0002 |
| 1.0 | ... | 0.0606 | 0.0608 | +0.0002 | ... | 1.5 | 0.1818 | 0.1812 | -0.0006 |
| 1.0 | ... | 0.1212 | 0.1212 | 0.0000 | 2.5 | ... | 0.0606 | 0.0608 | +0.0002 |
| 1.0 | ... | 0.1818 | 0.1814 | -0.0004 | 2.5 | ... | 0.1212 | 0.1197 | -0.0015 |
| 1.0 | ... | 0.2424 | 0.2414 | -0.0010 | ... | 2.5 | 0.0606 | 0.0608 | +0.0002 |
| 1.0 | ... | 0.3030 | 0.3011 | -0.0019 | ... | 2.5 | 0.1212 | 0.1200 | -0.0012 |

All the low results of this series were caused by a partial oxidation of ferrous iron by the iodic acid, more or less iodine being visible at the end of the five-minute period preceding titration. In no case was iodine liberated at once. These results indicate that the solution should not have an acidity with sulfuric or phosphoric acid greater than normal and that not more than 0.1 g. of ferrous iron should be added in excess, if five minutes are to be allowed to intervene between the time of adding the excess of iron salt and titration of that excess with permanganate. However, much larger quantities of both ferrous iron and sulfuric or phosphoric acids can be present if the excess of ferrous iron is titrated immediately.

Table II gives the results of actual analyses of known amounts of potassium iodide, thus showing the combined effect of manganese dioxide and potassium iodate on the decomposition of potassium permanganate and also obtaining a further check on the reduction of iodic acid by ferrous iron. The potassium iodide was measured into an Erlenmeyer flask, and 1 cc. of N NaOH added, followed by the permanganate. The solution was heated to boiling and kept just below ebullition for the time designated. After cooling in running water the mixed solution of 50 cc. of

¹ Computed on the basis of three replaceable H atoms.

ferrous sulfate (1 cc. = 0.802 cc. KMnO_4) plus 25 cc. of manganese preventive solution (60 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and 250 cc. H_3PO_4 of sp. gr. 1.70 per liter) was added. The time interval of standing previous to titration was about ten minutes in each experiment. No iodine was visible before titration, which showed that no reduction of iodic acid had taken place.

TABLE II.—PERMANGANATE DETERMINATION OF IODIDE IN PURE POTASSIUM IODIDE.

1 cc. KMnO_4 = 0.005648 g. Fe = 0.002798 g. KI.

1 cc. KMnO_4 = 0.8020 cc. FeSO_4 .

0.01 N KI = 1.66 g. KI per liter.

| | 0.01 N KI. Cc. | KMnO_4 . Cc. | Time. Min. | KMnO_4 required for excess. Cc. | KMnO_4 required for FeSO_4 . Cc. | KMnO_4 required for KI. Cc. | G. KI. | |
|--------|-------------------|--------------------------|---------------|---|---|---|----------|--------|
| | | | | | | | Present. | Found. |
| 1..... | 50 | 60 | 5 | 9.60 | 40.10 | 29.50 | 0.0830 | 0.0825 |
| 2..... | 50 | 60 | 15 | 9.64 | 40.10 | 29.54 | 0.0830 | 0.0827 |
| 3..... | 50 | 60 | 30 | 9.64 | 40.10 | 29.54 | 0.0830 | 0.0827 |
| 4..... | 50 | 60 | 60 | 9.64 | 40.10 | 29.54 | 0.0830 | 0.0827 |

The two preceding tables of results allow at least three conclusions: (a) the loss due to heating of the alkaline solution is negligible, (b) the reducing action of ferrous iron on the iodic acid can be made inappreciable, and (c) accurate determinations of iodide can be made by using the mixed solution containing some manganese salt and ferrous sulfate to remove the excess of permanganate as well as the hydrated manganese dioxide, the excess of ferrous iron being subsequently titrated with permanganate.

TABLE III.—PERMANGANATE DETERMINATION OF IODIDE IN MIXTURES WITH CHLORIDE AND BROMIDE.

1 cc. KMnO_4 = 0.005648 g. Fe.

1 cc. KMnO_4 = 0.8275 cc. FeSO_4 .

1 cc. KI = 0.00166 g. KI.

| | 0.1 N KBr. Cc. | 0.1 N NaCl. Cc. | MnSO_4 . Cc. | H_3PO_4 . Cc. | KI—Gram. | | |
|---------|-------------------|--------------------|--------------------------|----------------------------------|----------|--------|---------|
| | | | | | Present. | Found. | Error. |
| 1..... | 10 | .. | 10 | 15 | 0.0830 | 0.0828 | —0.0002 |
| 2..... | 30 | .. | 10 | 15 | 0.0830 | 0.0827 | —0.0003 |
| 3..... | 60 | .. | 10 | 15 | 0.0830 | 0.0828 | —0.0002 |
| 4..... | 100 | .. | 10 | 15 | 0.0830 | 0.0831 | +0.0001 |
| 5..... | 5 g. KBr. | .. | 10 | 15 | 0.0830 | 0.0828 | —0.0002 |
| 6..... | 10 " | " | 50 | 15 | 0.0830 | 0.0838 | +0.0008 |
| 7..... | 20 " | " | 100 | 25 | 0.0830 | 0.0827 | —0.0003 |
| 8..... | .. | 50 | 10 | 15 | 0.0830 | 0.0827 | —0.0003 |
| 9..... | .. | 10 g. NaCl | 50 | 25 | 0.0830 | 0.0827 | —0.0003 |
| 10..... | 50 | 50 | 10 | 15 | 0.0017 | 0.0018 | +0.0001 |
| 11..... | 50 | 50 | 10 | 15 | 0.0033 | 0.0035 | +0.0002 |
| 12..... | 50 | 50 | 10 | 15 | 0.0083 | 0.0086 | +0.0003 |
| 13..... | 50 | 50 | 10 | 15 | 0.0166 | 0.0168 | +0.0002 |
| 14..... | 50 | 50 | 10 | 15 | 0.0415 | 0.0414 | —0.0001 |
| 15..... | 50 | 50 | 10 | 15 | 0.0830 | 0.0827 | —0.0003 |

In Series III 50 cc. portions of 0.01 *N* potassium iodide solution were treated in an Erlenmeyer flask with permanganate in excess in the presence of bromides and chlorides, added in the form of 0.1 *N* potassium bromide and 0.2 *N* sodium chloride, or of the solids. One cc. of *N* sodium hydroxide was added, the solution heated and potassium permanganate added until there was about 10 cc. excess, then the solution was heated for about five minutes. The solution was cooled, and the ferrous sulfate solution (containing 250 g. per liter of manganous sulfate) was added in sufficient quantity to be about 10 cc. in excess. After complete solution of the manganese dioxide, phosphoric acid (1:3) was added. The excess of ferrous iron was then titrated with the permanganate.

In sample 6 the end point was blurred because of liberation of free bromine, the odor of which was distinct. MnSO_4 was not present in sufficient amount to take care of the large amount of KBr added originally. In other titrations concordant results were obtained.

In Series IV, 0.001 *N* potassium iodide was used with 0.001 *N* permanganate and 0.001 *N* ferrous sulfate. The method of procedure was the same as with 0.01 *N* potassium iodide. 1 cc. of *N* sodium hydroxide and 5 cc. of preventive solution (200 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and 350 cc. H_3PO_4 of sp. gr. 1.7 per liter) were employed in each case. The total volume was 100 cc. for each titration. Considerable care was found to be necessary to exclude foreign impurities when dealing with such weak solutions of permanganate. Only recently boiled water, previously distilled from alkaline permanganate, was employed. The titrations were continued carefully to the first definite pink color and the amount of permanganate necessary to give the same pink color in a blank experiment was subtracted.

TABLE IV.—PERMANGANATE DETERMINATION OF SMALL AMOUNTS OF IODIDE IN HALIDE MIXTURES.

| | 0.1 <i>N</i> KBr. Cc. | 0.1 <i>N</i> NaCl. Cc. | KI—Gram. | | |
|--------|--------------------------|---------------------------|----------|---------|----------|
| | | | Present. | Found. | Error. |
| 1..... | 5 | 5 | 0.00017 | 0.00016 | —0.00001 |
| 2..... | 5 | 5 | 0.00033 | 0.00033 | 0.00000 |
| 3..... | 5 | 5 | 0.00083 | 0.00080 | —0.00003 |
| 4..... | 5 | 5 | 0.00166 | 0.00167 | +0.00001 |
| 5..... | 5 | 5 | 0.00083 | 0.00082 | —0.00001 |

Correct results are thus seen to be possible with very small quantities of iodides.

2. The Iodimetric Titration of Iodate formed by the Permanganate Oxidation.

During the study of the permanganate titration of iodides, potassium iodide was added in a number of instances to the solution after the final titration of the excess of ferrous sulfate with permanganate and the resulting iodine titrated with standard thiosulfate. The results obtained

were surprisingly accurate. Consequently the author decided to study the factors influencing this titration.

The first point of interest is naturally the effect of ferric iron on potassium iodide in the acid medium necessary for the liberation of iodine by the interaction of iodic and hydriodic acids.

Tenth-normal potassium iodate (3.5678 g. pure KIO_3 per liter), ferric chloride (1 cc. = 0.006374 g. Fe) slightly acid with hydrochloric acid, ferrous sulfate solution (1 cc. = 0.004528 g. Fe), slightly acid with sulfuric acid, 5 *N* hydrochloric acid, 10 *N* sulfuric acid, 10 *N* phosphoric acid (computed on basis of 3 replaceable hydrogen atoms), manganese preventive solution containing 200 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ and 340 cc. H_3PO_4 (sp. gr. 1.7) per liter, *N* potassium iodide, and 0.1055 *N* sodium thiosulfate were used in the experiments of Table V. The letter *s* designates

TABLE V.—REACTION BETWEEN FERRIC IRON AND POTASSIUM IODIDE IN SULFURIC AND PHOSPHORIC ACID SOLUTIONS.

FeCl_3 = 0.006374 g. Fe per cc.

FeSO_4 = 0.004528 g. Fe per cc.

$\text{Na}_2\text{S}_2\text{O}_3$ = 0.1055 *N*.

5 cc. of normal KI solution used in each experiment.

| | FeCl ₃ . Cc. | FeSO ₄ . Cc. | 0.1 <i>N</i> KIO ₃ . Cc. | Normality. | | | Mn preven- tive solution. Cc. | Vol. Cc. | Na ₂ S ₂ O ₃ . Cc. | Time. Min. |
|----|----------------------------|----------------------------|---|----------------------------------|----------------------------------|------|-------------------------------------|-------------|--|-----------------|
| | | | | H ₂ PO ₄ . | H ₂ SO ₄ . | HCl. | | | | |
| 1 | 20 | ... | .. | 0.5 | .. | .. | .. | 100 | 0.10s | 10 |
| 2 | 20 | ... | .. | 1.0 | .. | .. | .. | 100 | 0.04s | 10 |
| 3 | 20 | ... | .. | 2.0 | .. | .. | .. | 100 | 0.04s | 10 |
| 4 | 20 | ... | .. | 2.0 | .. | .. | .. | 100 | 0.04 | 10 |
| 5 | 20 | ... | .. | 0.25 | .. | .. | .. | 200 | 0.04s | 10 |
| 6 | 20 | ... | .. | 0.125 | .. | .. | .. | 400 | 0.04s | 20 |
| 7 | 20 | ... | .. | 0.5 | .. | .. | .. | 200 | 0.04s | 20 |
| 8 | 20 | ... | .. | 0.25 | .. | .. | .. | 400 | 0.04s | 34 ¹ |
| 9 | 20 | ... | .. | .. | 1.0 | .. | .. | 100 | 5.00 | 2 |
| 10 | 20 | ... | .. | .. | 0.25 | .. | .. | 400 | 4.50s | 20 |
| 11 | 20 | ... | .. | .. | .. | .. | 5 | 100 | 0.04s | 10 |
| 12 | 20 | ... | .. | .. | .. | .. | 10 | 100 | 0.04s | 10 |
| 13 | 20 | ... | .. | .. | .. | .. | 5 | 200 | 0.04s | 10 |
| 14 | 20 | ... | .. | .. | .. | .. | 5 | 400 | 0.04s | 55 ¹ |
| 15 | 20 | ... | .. | .. | .. | .. | 10 | 400 | 0.04s | 72 ¹ |
| 16 | .. | 50 | .. | .. | .. | .. | 10 | 200 | 0.00s | 60 |
| 17 | .. | 50 ² | .. | .. | .. | .. | 10 | 200 | 0.04s | 10 |
| 18 | .. | ... | 30 | .. | .. | .. | 10 | 200 | 28.44s | Immediately |
| 19 | .. | ... | 50 | .. | .. | .. | 10 | 200 | 47.44s | Immediately |
| 20 | .. | ... | 30 | 5.0 | .. | .. | .. | 200 | 28.44s | Immediately |
| 21 | .. | ... | 30 | .. | .. | 5 | .. | 200 | 28.46s | Immediately |
| 22 | .. | ... | 30 | .. | .. | .. | 5 | 200 | 28.44s | Immediately |
| 23 | 20 | ... | 30 | .. | .. | .. | 5 | 200 | 28.46s | Immediately |
| 24 | 20 | ... | 30 | .. | .. | .. | 10 | 200 | 28.44s | Immediately |

¹ At end of 20 minutes starch solution was added and a drop of thiosulfate (0.04 cc.) and the remainder of the time was required for a very faint blue color to reappear.

² Oxidized with permanganate, then 1 cc. of ferrous sulfate was added in excess.

the experiments in which starch was used as indicator. When starch was not used, the bleaching of the iodine color of the solution was taken as the end point.

This series (Experiment 2) shows that normal phosphoric acid is capable of decreasing the speed of reaction between over a tenth of a gram of ferric iron and 0.05 *N* potassium iodide in a volume of 100 cc. at room temperature (21°) to such an extent that it becomes negligible for one or two minutes, only amounting to 0.04 cc. of 0.1 *N* thiosulfate in ten minutes. A considerable increase of the concentration of phosphoric acid, even to 4 *N*, does not change the speed of reaction sufficiently to give a measurable difference of volume of thiosulfate required by the method employed. Dilution of the normal solution to 400 cc. (Experiment 8), thus diminishing the concentration of all the reagents involved, causes a still slower rate of reaction. Sulfuric acid (Experiments 9 and 10) can not be substituted for phosphoric acid, since its action toward decreasing the rate of reaction is not commensurate with the latter. The preventive solution containing phosphoric acid (Experiments 11-15) employed in the permanganate determination of iodides exerts the same influence as phosphoric acid itself. Experiment 16 shows that ferrous iron is without effect. Experiments 18 to 22 show that iodic acid can be titrated quantitatively in the presence of the phosphoric acid or preventive solution, and Experiments 23 and 24 show that the ferric chloride has no influence on the titration of iodic acid, if the titration is performed immediately after adding the potassium iodide.

Definite samples of potassium iodide were taken in the Series VI and varied quantities of potassium bromide and sodium chloride added to each, after which the sample was analyzed for iodine by the permanganate method as previously outlined and the result recorded. Ferrous sulfate solution was then added in slight excess, followed by 5 cc. of *N* KI, and the free iodine titrated immediately with standard thiosulfate adding 1 cc. of 1% starch solution when the solution became very faintly yellow in order to get the sharp iodine-starch end point. The permanganate, ferrous sulfate and thiosulfate solutions used in this series were tenth-normal and the potassium iodide was hundredth-normal.

Table VII includes results obtained using 0.001 *N* solutions. The 0.001 *N* KMnO_4 is thousandth-normal compared with KI as standard. Reacting with iron in acid solution this permanganate would be 0.01 *N* inasmuch as 2KMnO_4 or $\text{K}_2\text{Mn}_2\text{O}_8$ will react with 10 Fe in acid solution but will only oxidize one molecule of KI to KIO_3 in alkaline solution. Hence the permanganate contains 0.316 g. of potassium permanganate per liter. The same relative strength obtains for the ferrous sulfate solution used in this series. The thiosulfate solutions used in this work were standardized against pure potassium iodate, referring the normality

PERMANGANATE AND IODIMETRIC DETERMINATION OF IODIDE 1495

strength of the thiosulfate (0.001 *N*) to potassium iodide as a basis rather than to the iodate. The same precautions used in Series IV are necessary here to avoid any slight impurities of oxidizing or reducing character in the permanganate determination. The manganese solution used in these two series contained 200 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ + 350 cc. of H_3PO_4 (sp. gr. 1.7). In Table VI 15 cc. and in Table VII 5 cc. of this solution were added in each experiment.

TABLE VI.—IODIMETRIC DETERMINATION OF IODIDE IN HALIDE MIXTURES.

| | Present—Gram. | | Total volume. Cc. | KI—Gram. | | |
|--------|---------------|--------|-------------------------|----------|---------------------|---|
| | KBr. | NaCl. | | Present. | Found by | |
| | | | | | KMnO ₄ . | Na ₂ S ₂ O ₄ . |
| 1..... | 0.5953 | 0.5851 | 300 | 0.0830 | 0.0828 | 0.0827 |
| 2..... | 0.5953 | 0.5851 | 300 | 0.0830 | 0.0827 | 0.0826 |
| 3..... | 0.5953 | 0.5851 | 300 | 0.0830 | 0.0829 | 0.0826 |
| 4..... | 0.5953 | 0.5851 | 300 | 0.0415 | 0.0414 | 0.0415 |
| 5..... | 0.5953 | 0.5851 | 250 | 0.0415 | 0.0412 | 0.0415 |
| 6..... | 0.5953 | 0.5851 | 200 | 0.0166 | 0.0168 | 0.0165 |
| 7..... | 0.5953 | 0.5851 | 200 | 0.0083 | 0.0082 | 0.0080 |
| 8..... | 0.5953 | 0.5851 | 200 | 0.0017 | 0.0018 | 0.0016 |

TABLE VII.—IODIMETRIC DETERMINATION OF SMALL AMOUNTS OF IODIDE IN HALIDE MIXTURES

| | Present—Gram. | | Total volume. Cc. | KI—Gram. | | |
|--------|---------------|--------|-------------------------|----------|---------------------|-----------------------------------|
| | KBr. | NaCl. | | Present. | Found by | |
| | | | | | KMnO ₄ . | Na ₂ SO ₄ . |
| 1..... | 0.0595 | 0.0585 | 200 | 0.00830 | 0.00825 | 0.00825 |
| 2..... | 0.0595 | 0.0585 | 200 | 0.00830 | 0.00832 | 0.00826 |
| 3..... | 0.0595 | 0.0585 | 100 | 0.00415 | | 0.00414 |
| 4..... | 0.0595 | 0.0585 | 100 | 0.00166 | 0.00169 | 0.00170 |
| 5..... | 0.0238 | 0.0234 | 100 | 0.00083 | 0.00084 | 0.00086 |
| 6..... | 0.0238 | 0.0234 | 100 | 0.00033 | 0.00033 | 0.00033 |
| 7..... | 0.0119 | 0.0117 | 100 | 0.00017 | 0.00017 | 0.00017 |

These two series show that the iodimetric titration of the iodate in the residual solution from the permanganate method is accurate if the solution contains sufficient phosphoric acid to prevent the action of ferric iron on potassium iodide. Naturally if the permanganate data are not desired they can be neglected and only the thiosulfate titration computed. The iodimetric method is to be preferred when titrating such small amounts of iodine as the samples of Series VII contained, essentially because of the sharpness of the starch iodine end point contrasted with that of permanganate and of the lesser effect of slight impurities such as oxygen in water on the final titration with the thiosulfate.

The following procedure is well adapted to the analysis of a halogen mixture for its iodine content. One-twentieth to five grams of sample,¹

¹ If as small a sample as 0.05 g. is desired a larger portion should be weighed out and an aliquot analyzed, for example, 0.5 g. diluted to 500 cc. and a 50 cc. portion used in the analysis.

depending upon the amount of iodine present, is dissolved in 100 cc. of recently boiled distilled water in an Erlenmeyer flask, 1 cc. of *N* sodium hydroxide added, the solution is heated to boiling and standard permanganate added, 5-10 cc. at a time with continuous shaking, allowing several seconds between each addition before observing the color of the solution. If the solution becomes cooled it is reheated and the additions are continued until a distinct color (red or green) is imparted to the solution. The flask is covered with a small watch glass and the liquid then heated just below boiling for about five minutes. If the color disappears, more permanganate is added and the solution reheated. It is then cooled in running water and to it is added, all at once, with agitation of the solution, a mixture of 15 cc. of manganese preventive solution (200 g. $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ + 350 cc. H_3PO_4 , of sp. gr. 1.7, per liter) and sufficient standard ferrous sulfate to react with all the manganese dioxide and excess of permanganate and have an excess of ten to fifteen cubic centimeters. As soon as the manganese dioxide has dissolved completely the solution is diluted to 300-400 cc. and titrated with the permanganate¹ to the first appearance of a faint pink color. A smaller amount of preventive solution can be added and a smaller volume used with small quantities of iodine involved. The percentage of iodine is calculated from the amount of permanganate required to oxidize the iodide to iodate.

For the iodimetric titration a few drops of ferrous sulfate are added to bleach out any excess of permanganate, followed by 5 cc. of *N* KI solution (free from iodine) or 1 g. of solid,¹ after which the iodine is titrated immediately with standard thiosulfate. The percentage of iodine or iodide is then computed from the amount of thiosulfate required to react with the iodine produced by the reduction of the iodate to iodide.

The two methods have about equal merit, except when applied to extremely small quantities of iodides, when the iodimetric method is preferable. If the iodimetric method only is to be followed, naturally the strength of the permanganate and ferrous sulfate solutions need not be known exactly.

Summary.

1. In the original method of Pean de St. Gilles for titrating iodide, in the presence of bromide and chloride with permanganate the results are erroneous because of the formation of free bromine, chlorine or hypochlorous acid.

¹ No iodine color should be visible before titration with permanganate or before the addition of potassium iodide prior to the thiosulfate titration. If such a color develops, the proper adjustment has not been made between an exceptionally high concentration of ferric iron and phosphoric acid or too long a time has intervened between the time of finishing the permanganate and starting the thiosulfate titration, in which case another sample must be analyzed, using a greater dilution and correspondingly more preventive solution or phosphoric acid.

2. The presence of manganese sulfate and phosphoric acid in the ferrous solution allows the removal of the excess of permanganate and manganese dioxide without liberation of bromine or chlorine from the halides. Likewise the manganese and phosphoric acid insure a correct permanganate titration of the ferrous iron excess.

3. Iodide can also be determined in the presence of bromide and chloride by addition of potassium iodide to the final solution obtained as in 2 and titration of the liberated iodine with thiosulfate.

4. Both titrations can be made on a single sample, using the residual solution from the permanganate titration for the iodimetric determination.

Very small amounts of iodine are best determined by the iodimetric method. With moderate quantities of iodine both methods outlined are easy of manipulation, rapid in execution and accurate.

MADISON, WISCONSIN.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK.]

THE PRECIPITATION OF PHOSPHORUS AS AMMONIUM PHOSPHOMOLYBDATE IN THE PRESENCE OF SULFURIC ACID.

By K. GEORGE FALK AND KANEMATSU SUGIURA.

Received March 20, 1915.

The Neumann method for the determination of phosphorus in organic matter is based upon the oxidation of the material by a mixture of concentrated sulfuric and nitric acids, precipitation of the phosphorus as ammonium phosphomolybdate, and titration of the latter, after removal of ammonia, with standard sodium hydroxide solution. The formula of the phosphomolybdate precipitate has been taken to be essentially $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 2\text{HNO}_3$ under the conditions described by Neumann,¹ Gregerson,² and others. A substance possessing this formula, after the removal of ammonia either by boiling in alkaline solution or by combination with formaldehyde,³ would require 56 equivalents of sodium hydroxide per gram molecule of P_2O_5 to be neutral toward phenolphthalein. If the precipitate is titrated with 0.5 *N* NaOH solution, one cc. would be equivalent to 1.268 mg. P_2O_5 or 0.553 mg. P; on the other hand, if it is dried at 110–120° before titrating, the nitric acid would be driven off and then one cc. would be equivalent to 1.365 mg. P_2O_5 .

The possibility of the composition of the precipitate varying under different conditions has been indicated a number of times,⁴ but the good

¹ *Z. physiol. Chem.*, **37**, 115 (1902); **43**, 35 (1904).

² *Ibid.*, **53**, 453 (1907).

³ Bang, *Biochem. Z.*, **32**, 443 (1911).

⁴ Recently by Hibbard, *J. Ind. Eng. Chem.*, **5**, 998 (1913), who also gives a very complete bibliography. Cf. also A. E. Taylor and C. W. Miller, *J. Biol. Chem.*, **18**, 215 (1914).

results obtained in practice with the factor given by Neumann appeared to substantiate the formula ascribed. Recently, however, Heubner¹ found this factor to be too small and adopted the value 0.57 mg. in place of 0.553 mg. for the quantity of phosphorus equivalent to one cc. 0.5 *N* NaOH solution.

The work described in this paper developed from the study of the phosphorus determinations made in connection with enzyme investigations in this laboratory, and deals especially with the part played by sulfuric acid in the precipitation of the phosphomolybdate.

A number of different standard phosphate solutions were used. The experiments to be described were made with sodium ammonium phosphate 10.88 g. of $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (Kahlbaum's "zur Analyse") were dissolved in water and diluted to two liters. Two different solutions, designated I and II were made up at different times. The methods of analysis used will first be given.

A. Molybdate Method, no Sulfuric Acid Present.²—To the phosphate solution (generally 25 cc.) 12 cc. ammonium nitrate solution (750 g. NH_4NO_3 dissolved and diluted to 1 liter) and 50 cc. molybdate solution (60 g. MoO_3 , 440 cc. H_2O , 60 cc. NH_4OH , sp. gr. 0.90, poured into a mixture of 250 cc. H_2O and 250 cc. HNO_3 , sp. gr. 1.40, filtered after standing several days) were added, the mixture heated at 80° on a water bath for 10 minutes, cooled, and allowed to stand over night. It was then filtered on asbestos in a Gooch crucible, washed 5–6 times with an NH_4NO_3 solution (containing 50 g. of the salt and 10 cc. conc. HNO_3 in 1 liter), once with 1% HNO_3 solution, dried in an air oven at 120° and weighed as $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$.

B. Magnesium Ammonium Phosphate.—To 25 cc. of the phosphate solution, 10 cc. magnesia mixture (containing 55 g. cryst. magnesium chloride, 70 g. NH_4Cl , and 300 cc. NH_4OH , sp. gr. 0.96, diluted to 1 liter and filtered) were added, the mixture heated to boiling and 5 cc. 3 *N* NH_4OH solution added drop by drop; stirred, allowed to stand over night and filtered through a Gooch crucible with asbestos (or through an ashless paper). The precipitate was washed with 2.5% ammonia solution, dried, ignited to constant weight (after addition of conc. HNO_3) over a Meker burner, and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

C. Ignition Method.—50 cc. of the solution were evaporated to dryness in a platinum dish at 100° in an air oven; the residue was then ignited to constant weight over a Meker burner and weighed as NaPO_3 .

D. Neumann Method.—To the phosphate solution were added the stated amounts of conc. H_2SO_4 , sp. gr. 1.84, water, and 50% NH_4NO_3 solution, the mixture heated to 75° and the stated quantity of a 10%

¹ *Biochem. Z.*, 64, 393 (1914).

² Cf. for instance, Olsen, "Quantitative Chemical Analysis" 1910, p. 119.

ammonium molybdate solution (from Merck's product, highest purity) added with stirring. After 15 minutes, the mixture was cooled and either filtered at once or allowed to stand over night and then filtered.

DI. Weighing the Precipitate.—The precipitate was filtered on a Gooch crucible (asbestos), washed 7 times (unless otherwise stated) with 5–10 cc. ice-cold water each time, and dried at 120° in an air oven.

DII. Titrating the Precipitate.—The phosphomolybdate precipitate obtained as described in Method D was filtered on a Gooch crucible or on paper, washed with ice-cold water as described in DI, then the paper or the Gooch crucible containing the wet precipitate was returned to the beaker in which the precipitation had been made. If the phosphomolybdate precipitate had been dried and weighed as in Method DI, the Gooch crucible with the precipitate was placed in a beaker. The subsequent treatment of the wet or dry precipitate was the same, namely, 30 cc. water were added, then 45 cc. 0.5 *N* NaOH solution with stirring until all had dissolved; the solution was then either boiled for at least 30 minutes until litmus paper showed no further evolution of ammonia, cooled, made acid with 0.5 *N* H_2SO_4 solution, and titrated with 0.5 *N* NaOH solution using phenolphthalein as indicator; or, 50 cc. 30% formaldehyde solution, neutralized toward phenolphthalein, were added, the mixture allowed to stand 5 minutes, 7 cc. (or other suitable amount) 0.5 *N* H_2SO_4 solution added, and the solution titrated to alkaline reaction with 0.5 *N* NaOH solution.

E. Reprecipitation as Phosphomolybdate.—The weighed precipitate (from A or D, DI) was treated in a beaker with 50 cc. H_2O and 3 cc. conc. ammonia solution, warmed, filtered through paper, and washed successively with 2.5% ammonia solution and water. To the filtrate were added 20 cc. 50% NH_4NO_3 solution, and 1 cc. 10% ammonium molybdate solution. The mixture was heated on an electric stove until bubbles began to rise, and 20 cc. warm nitric acid (3 parts conc. to 1 part water) added drop by drop with stirring. It was then cooled, and after standing over night treated as in Method A.

F. Reprecipitation as Magnesium-Ammonium Phosphate.—The phosphomolybdate precipitate was transferred to a beaker, dissolved in ammonia (Method E), acidified with conc. HCl , and made slightly alkaline with ammonia; 10 cc. of the magnesia mixture (Method B) were then added, the mixture heated to boiling, cooled, and 20 cc. conc. ammonia solution added. After standing over night, the precipitate was filtered, etc., as in Method B.

G. Lead Molybdate.¹—The phosphomolybdate precipitate was dissolved in ammonia (Method E), diluted to 100 cc. and 25 cc. portions taken for analysis. Each portion was diluted with 50 cc. H_2O , and 22 cc.

¹ Raper, *Biochem. J.*, 8, 649 (1914).

conc. HCl, followed by 20 cc. of 4% lead acetate solution and 200 cc. of a mixture of equal parts of 50% ammonium chloride and 50% ammonium acetate solutions added. After standing over night, the precipitate was filtered on a Gooch crucible (asbestos), washed with hot water 10 times (the wash water was somewhat turbid up to the sixth washing), then dried, ignited over a Meker burner, and weighed as PbMoO_4 .

The results will be given as mg. P_2O_5 in 25 cc. solution, since this was the quantity used in the analyses. The phosphate contents of the two solutions were first determined by the standard methods. Four analyses of 25 cc. portions of Solution I by Method A gave 1.2338–1.2394 g. phosphomolybdate when dried at 120° , or a mean content of 46.8 mg. P_2O_5 . Two of these precipitates, titrated by Method DII (formaldehyde), gave the same value (factor 1.365). Four analyses by Method B, filtered on a Gooch crucible, gave 0.0730–0.0742 g. $\text{Mg}_2\text{P}_2\text{O}_7$, or 46.8 mg. P_2O_5 as mean, and two analyses, filtered on paper, 0.0715–0.0728 g. $\text{Mg}_2\text{P}_2\text{O}_7$, or 46.0 mg. P_2O_5 . By Method C, 50 cc. portions gave 0.1336 and 0.1337 g. NaPO_3 , or 46.5 mg. P_2O_5 per 25 cc. Solution I contained, therefore, as the mean, very nearly 46.8 mg. P_2O_5 per 25 cc., taking into account the number of the determinations by each method, and the separate deviations. Four 25 cc. portions of Solution II by Method A gave 1.2350–1.2401 g. phosphomolybdate, mean P_2O_5 content 46.8 mg.; two portions precipitated by Method A, then dissolved without drying and reprecipitated by Method E, gave 1.2455 and 1.2469 g. phosphomolybdate, mean 47.1 mg. P_2O_5 . These last two precipitates titrated by Method DII (formaldehyde) required 34.91 and 34.92 cc. 0.5 *N* NaOH solution, or 47.7 mg. P_2O_5 as mean. Solution II may, therefore, be taken as containing very nearly 47.1 mg. P_2O_5 per 25 cc.

A number of experiments which will not be given in detail showed that the titration of the phosphomolybdate precipitate by Method DII gave the same results whether the ammonia was removed by boiling or was combined with formaldehyde. The same results were also obtained whether the precipitates were filtered on paper or on asbestos in a Gooch crucible.

Four 25 cc. portions of Solution I by Methods D and DII, with 5 cc. conc. sulfuric acid, 8 cc. NH_4NO_3 solution, and 40 cc. molybdate solution required 37.33–37.51 cc. 0.5 *N* NaOH solution. Assuming the formula $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 2\text{HNO}_3$ and the factor 1.268, this corresponds to an average of 47.6 mg. P_2O_5 . One portion of the same mixture by Methods D and DI gave 1.3565 g. phosphomolybdate, which, when titrated by Method DII required 37.36 cc. 0.5 *N* NaOH solution. Assuming no HNO_3 in the dried precipitate, these values correspond to 51.3 and 51.0 mg. P_2O_5 , respectively. It will be noted, however, that the titration values are the same, whether or not the phosphomolybdate precipitate

was dried before titrating. This was observed in every case. With mixtures containing 5 cc. sulfuric acid, 20 cc. ammonium nitrate solution, and 40 cc. molybdate solution, Methods D and DII, direct titration of the undried precipitate, gave 36.12 and 36.14 cc. 0.5 *N* NaOH solution, corresponding to 45.9 mg. P_2O_5 (1.268 factor). The same mixture by Methods D and DI, after drying and weighing the phosphomolybdate precipitate, gave 49.5 mg. P_2O_5 , and titrating this dried precipitate 36.16 cc. With 50 cc. NH_4NO_3 solution, 70 cc. H_2O and the rest of the mixture the same, 35.80–35.88 cc. 0.5 *N* NaOH solution were required for the undried precipitates, or 45.5 mg. P_2O_5 , assuming HNO_3 to be present. This value is considerably lower than the standard value (46.8), but, assuming no nitric acid to be present in the precipitate, would give 48.9 mg. P_2O_5 , a value much too large. The filtrates from these last precipitates, on being neutralized with ammonia, acidified with nitric acid, and 15 cc. conc. nitric acid in excess added, gave no further precipitate. The results with 5 cc. conc. sulfuric acid showed that drying the precipitate had no effect on the titration, and that the results were either too large or too small, depending upon the amount of ammonium nitrate added. In the ordinary Neumann wet combustion method, often more than 5 cc. conc. sulfuric acid are present. A number of experiments were, therefore, made with the following mixture: 25 cc. Solution I, 10 cc. conc. sulfuric acid, 65 cc. H_2O , 50 cc. ammonium nitrate solution, and 40 cc. molybdate solution. Eight determinations by Methods D and DII required 35.55 to 36.02 cc. 0.5 *N* NaOH solution, giving a mean value 45.5 mg. P_2O_5 (factor 1.268). Assuming no nitric acid present in the precipitate, the value 48.9 mg. P_2O_5 (factor 1.365) is obtained. Four portions of the same mixture by Methods D and DI gave 1.2985 to 1.3047 g. phosphomolybdate precipitate, or 49.2 mg. P_2O_5 (for the formula $(NH_4)_3PO_4 \cdot 12MoO_3$). These precipitates when titrated by Method DII required 35.83 to 36.03 cc. 0.5 *N* NaOH solution, or very nearly the amounts required by the undried precipitates. With the factor 1.268 this corresponds to 45.5 mg. P_2O_5 ; with the factor 1.365 to 49.0 mg. P_2O_5 . The filtrates from these precipitates, neutralized with ammonia, acidified with nitric acid and 15 cc. conc. nitric acid in excess added, gave no further precipitate on standing. A few experiments in which more sulfuric acid was present, were made. Using 12.5 cc. conc. sulfuric acid in place of 10 cc., determinations by Methods D and DII required 34.81 and 35.29 cc. 0.5 *N* NaOH solution, while the filtrates, treated as described above, gave additional precipitates after standing over night, requiring 0.89 and 0.34 cc. The average total titration was 35.67 cc. With 15 cc. conc. sulfuric acid in place of 10 cc. the first precipitates required 28.83 and 30.13 cc., while from the filtrates were obtained precipitates requiring 7.70 and 6.53 cc. The average total titration was 36.60 cc., of which 15–20%

was obtained with the second precipitates. The total titrations with different amounts of sulfuric acid present were not in accord. This would appear to indicate a varying composition of the precipitates. With more than 10 cc. conc. sulfuric acid present, the precipitation was not complete. 50 cc. of the 50% NH_4NO_3 solution present in 190–195 cc. total solution is slightly more than the quantity recommended by Neumann, and somewhat less, 13% instead of 15%, than that recommended by Gregerson.

The experiments with Solution II were carried out with different ends in view, and the results obtained indicate some of the reasons for the irregularities observed by different workers. 25 cc. of this solution contained 47.1 mg. P_2O_5 as indicated before. The mixture used in all of the following work with this solution was made up of 25 cc. Solution II, 10 cc. conc. sulfuric acid, 50 cc. NH_4NO_3 solution, 65 cc. water, and 40 cc. molybdate solution.

The phosphomolybdate precipitate in the Neumann method must be washed with ice-cold water until the wash water is no longer acid. Two sets of two portions each, precipitated by Method D, then treated by Method DI, the first set washed four times with ice-cold water, the second seven times, gave 1.3079–1.3089 g. and 1.3042–1.3047 g. phosphomolybdate precipitate, respectively, corresponding to 49.5 and 49.3 mg. P_2O_5 . Two other sets of three portions each by Methods D and DII, washed four times and seven times, respectively, required 36.43–36.72 cc. and 36.11–36.27 cc. 0.5 *N* NaOH solution, respectively, corresponding to 46.3 and 46.0 mg. P_2O_5 with the factor 1.268, or 49.9 and 49.4 mg. P_2O_5 with the factor 1.365. The fourth washings required 2.44 cc. 0.5 *N* NaOH, the 7th 0.12 cc. 0.5 *N* NaOH. The washings tested for sulfuric acid gave, in a series of similar experiments, for the sixth washing a test equivalent to 0.2–0.3 cc. 0.1 *N* H_2SO_4 , and for the eighth washing a test equivalent to 0.02–0.05 cc. 0.1 *N* H_2SO_4 . After the sixth washing the phosphomolybdate precipitate began to run through the filter, as shown by the turbidity. Practically all the free acid was, therefore, removed by seven washings, but not by four. No volatile substance, such as nitric acid, is present in the precipitates, as shown by the agreement between the dried and undried precipitates.

A number of experiments involving solution of the phosphomolybdate and reprecipitation were made. Three portions by Methods D and DI gave 1.3087–1.3116 g. phosphomolybdate precipitate, corresponding to a mean P_2O_5 content of 49.5 mg. These precipitates dissolved and treated by Method F gave 0.0728–0.0732 g. $\text{Mg}_2\text{P}_2\text{O}_7$, corresponding to 46.6 mg. P_2O_5 . Another set of three by Methods D and DI gave 1.3137–1.3138 g. precipitate, corresponding to 49.7 mg. P_2O_5 ; these precipitates dissolved and reprecipitated by Method E gave 1.2561–1.2564 phosphomolybdate

precipitate, corresponding to 47.5 mg. P_2O_5 ; these dissolved and reprecipitated by Method F gave 0.0728–0.0732 g. $Mg_2P_2O_7$ or 46.5 mg. P_2O_5 .

These experiments show that the first precipitate of the phosphorus as phosphomolybdate from the solution containing sulfuric acid possesses a different composition from that of the precipitate obtained if little or no sulfuric acid is present. That no nitric acid is contained in the precipitate formed with sulfuric acid present in the solution is shown also by the fact that the same results were obtained whether or not the precipitates were dried at 120° . An attempt was, therefore, made to study the composition of these precipitates. The amount of sulfate in the precipitates was accordingly determined. Four portions of Solution II, with the same mixture as before, were treated by Methods D and DI. The precipitates were dissolved and reprecipitated by Method E; the mother liquors from these reprecipitations were evaporated to dryness on the water bath after the addition of one cc. conc. hydrochloric acid, 25 cc. water added, and the mixture filtered, the filtrates diluted to 100 cc. and 5 cc. concentrated hydrochloric acid and 5 cc. 10% $BaCl_2$ solution added while boiling. After the customary treatment, 0.0179–0.0214 g. $BaSO_4$ were obtained, equivalent to a mean value of 0.0080 g. H_2SO_4 . Similar treatment of Solution II without added sulfuric acid, by Methods A and E, gave 0.0001 and 0.0004 g. $BaSO_4$. These results appear to show that sulfuric acid is an essential part of the precipitate formed under the given conditions.

Based upon the amounts of phosphate and sulfate present, and upon a number of nitrogen and molybdenum determinations, the composition of the precipitate was calculated to be $4[(NH_4)_3PO_4 \cdot 12MoO_3] + (NH_4)_2SO_4 \cdot 5MoO_3$. The mean of four closely agreeing nitrogen determinations by the Kjeldahl method¹ of the precipitates obtained from Solution II by Methods D and DI was 2.23%; calculated for the above formula, 2.35% N. Several determinations of the molybdenum in these precipitates by Method G gave, for 25 cc. portions of the phosphomolybdate precipitate dissolved in 100 cc., 0.7627 and 0.7496 g. $PbMoO_4$, corresponding to an average of 90.6% MoO_3 . The calculated MoO_3 content for a substance of the above formula is 91.3%; for a substance of the formula $(NH_4)_3PO_4 \cdot 12MoO_3$, 92.1%. To check up the method, similar portions of the phosphomolybdate precipitate from Solution II by Method A without the addition of sulfuric acid, gave 0.7216 and 0.7326 g. $PbMoO_4$, or a mean MoO_3 content of 92.6%.

The precipitate is probably present as a complex compound and not as a mixture, since similar solutions containing no phosphoric acid gave no precipitate of sulfomolybdate. The formula found, as given above,

¹ Sherman, "Methods of Organic Analysis," 1912, p. 294.

naturally holds only for the precipitate formed under the given conditions. Under different conditions different proportions of sulfuric acid and molybdic oxide might be carried down, but the general relations would probably be similar. Thus, the carrying down of molybdic acid in excess of the 24 MoO_3 to one P_2O_5 has been observed at different times, recently by H. S. Halcro Wardlaw in a paper on the "Accuracy of Neumann's Method for the Estimation of Phosphorus."¹ That sulfate may be present in the precipitate has also been indicated at various times, but it was considered to replace the nitric acid which ordinarily forms part of the precipitate. The composition of the precipitates described in this paper have been given in the above form, because when no sulfuric acid was present, each P_2O_5 was combined with 24 MoO_3 . The sulfuric acid which was precipitated was, therefore, assumed to carry down the further portion of MoO_3 which was found.

If the precipitate, whose complete formula may be written $(\text{NH}_4)_{14}(\text{PO}_4)_4\text{SO}_4.53\text{MoO}_3$ is titrated with alkali after removal of the ammonia, each gram molecule of P_2O_5 would require 58 equivalents of NaOH , instead of the 56 required by two molecules of the precipitate $(\text{NH}_4)_3\text{PO}_4.12\text{MoO}_3.2\text{HNO}_3$. From a consideration of the phosphosulfomolybdate precipitate, it is evident that the proportion of sulfate, phosphate, and molybdenum in the complex may well be subject to considerable variation. If the same ratio for MoO_3 to sulfate precipitated with the phosphomolybdate holds, a smaller concentration of sulfuric acid in the solution would be expected to result in titration values six times smaller than if the amount of sulfate in the precipitate alone varied. This may account for the entirely different factor, corresponding to less than 56 equivalents NaOH per gram molecule P_2O_5 , found by Heubner, who worked with smaller amounts of phosphorus and sulfuric acid. Between these two sets of results lie those obtained by Neumann, Gregerson, and more recently by Greenwald.² These workers found the relation, 56 equivalents NaOH per gram molecule P_2O_5 , to hold for the P_2O_5 content of the phosphomolybdate precipitate for the conditions of precipitation chosen by them.

In the course of this investigation a number of other phosphate solutions, and also solutions containing widely different amounts of phosphate, were used. The results obtained bear out, in general, the conclusions given, but not enough work was done to determine the variation of the composition of the precipitate with different amounts of phosphate and sulfuric acid. Finally, it may be stated that the titration of the phosphomolybdate precipitate gives satisfactory results only if the conditions of precipitation have been worked out with known amounts of phosphate

¹ *J. Roy. Soc. New South Wales*, 48, 73 (1914).

² *J. Biol. Chem.*, 14, 369 (1913).

and an empirical factor determined. Otherwise, solution and reprecipitation of the phosphomolybdate precipitate are essential.¹

Conclusions.

The precipitate of ammonium phosphomolybdate formed in the presence of sulfuric acid (as in Neumann's method) contains sulfate apparently as an essential part of the molecule, together with an excess of molybdic oxide, and no nitric acid. The composition of this phosphosulfomolybdate precipitate may vary with the concentration of the different constituents in the solution. These variations explain the different factors found for the titration of the precipitate with alkali. The composition of the precipitate for a certain set of conditions was found to be $4[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3] + (\text{NH}_4)_2\text{SO}_4 \cdot 5\text{MoO}_3$.

FLUOBORIC AND FLUOSILICIC ACIDS IN THE QUALITATIVE ANALYSIS OF SODIUM.

By F. C. MATHERS, C. O. STEWART, H. V. HOUSEMANN AND I. E. LEE.

Received April 10, 1915.

The scheme for the detection of sodium is the only unsatisfactory test in the qualitative analysis of the soluble or alkali group of bases. The flame or spectrum test is so delicate that the quantity of sodium normally present in all reagents always distinctly gives it. This is confusing to inexperienced students. The pyroantimonate method has never given accurate results in this laboratory in the hands of beginning students. The following method is the final result of experiments which have been conducted by the authors for a number of years in an effort to devise a quick and accurate test for sodium.

Method of Analysis.—The filtrate containing the potassium, sodium, ammonium and magnesium (after the other metals have been removed in the ordinary way) is evaporated to dryness and ignited to remove the ammonium. The residue is dissolved in 10 cc. of water² by warming. A small portion of the solution (a few drops) is removed and tested for potassium with sodium cobaltic nitrite. The remainder of the solution is treated with an equal volume of alcohol and an excess of fluoboric acid in 50% alcohol. The potassium is completely precipitated as potassium fluoborate, a flocculent, easily filtered precipitate. Sodium and magnesium remain in solution. The sodium in the filtrate may then be precipitated with fluosilicic acid as sodium fluosilicate, a gelatinous, semi-transparent precipitate which settles slowly, consequently careful observation is necessary to detect it when only small quantities of sodium are present.

¹ Cf. Hibbard, Raper, and others.

² Ten cc. of water should be used for each gram of sodium and potassium chloride present.

Magnesium fluosilicate, a very soluble salt, does not precipitate, but potassium fluosilicate and sometimes ammonium fluosilicate are precipitated if the potassium and ammonium have not been previously removed. In the absence of sodium, a precipitate sometimes forms on long standing as a result of the action of hydrofluoric acid upon the glass, if any free hydrofluoric acid was present in the reagents.

Lithium does not interfere with the test for sodium, probably on account of slow precipitation or colloidal solution of the lithium fluosilicate of which only 4 parts dissolve in 100 of 46% alcohol (Comey). In some test solutions rich in lithium, a gel formed after 48 hours.

Preparation of Reagents.—Fluoboric acid is very easily made by adding an excess of boric acid to hydrofluoric acid in a lead or platinum dish. Thirty-five grams of boric acid to 100 g. of 48% hydrofluoric acid is generally sufficient, but boric acid should always be added until a test portion does not precipitate a lead nitrate solution. The solution, after cooling, is treated with an equal volume of alcohol and enough fluosilicic acid to precipitate any sodium which may have been introduced as an impurity in the boric acid. A large excess of the fluosilicic acid must be avoided.

Fluosilicic acid may be easily prepared by pouring hydrofluoric acid upon sand until the latter is barely covered. A wax bottle may be used because the heat of reaction is not great. The reaction is complete in a few hours but the solution should always be tested for free hydrofluoric acid. An equal volume of alcohol should be added before using.

The reagents must be kept in wax, rubber, lead or paraffin bottles or beakers. In the ordinary course of analysis, these reagents when properly made, do not noticeably etch the test tubes.

These reagents work just as satisfactorily when made from commercial as from pure hydrofluoric acid. The only difficulty is in the preparation where the impurities, *e. g.*, sulfates, interfere with the test for fluoride in determining the completeness of the change into fluoboric and fluosilicic acids.

Delicacy of Tests.—One milligram of sodium in 5 cc. of 50% alcohol gives a good test with fluosilicic acid. In the detection of smaller amounts of sodium, a smaller volume of solution must be used. If large amounts of potassium and only small amounts of sodium are present, the filtrate after the precipitation of the potassium with fluoboric acid, should be evaporated to dryness and ignited for an instant at a dull red heat. The residue should be dissolved in 50% alcohol (2–3 cc.), filtered and tested for sodium with the fluosilicic acid. In this way 2 mg. of sodium in 0.5 g. of potassium chloride was easily detected. Addition of 1 g. magnesium chloride in no way interfered with the test for the sodium. Correspond-

ing solutions containing no sodium gave no precipitate with the fluosilicic acid.

One mg. of sodium in 5 cc. of 50% alcohol was easily detected in a solution containing 0.1 g. of lithium as chloride and also in a solution containing 0.1 g. of lithium as chloride and 0.2 g. of potassium chloride. A blank, containing only lithium, gave no precipitate.

Pure fluoboric acid in 50% alcohol solution may be used as a test for potassium in place of sodium cobaltic nitrite or perchloric acid. Two milligrams of potassium in 5 cc. of 50% alcohol may be easily detected. The only objection to this test is that impure fluoboric acid, *e. g.*, when made from commercial hydrofluoric acid, sometimes gives a precipitate when potassium is absent; the cause of this was not investigated. The advantage of this test is that it is not interfered with by sodium and magnesium nor by ammonium and cyanides which interfere with the sodium cobaltic nitrite test. However, owing to the trouble of making pure fluoboric acid, the test for potassium with sodium cobaltic nitrite seems best wherever it can be used.

Use of Other Reagents.—Perchloric acid¹ is preferable to the fluoboric acid in this method but the latter is recommended because it is so much easier to prepare.

Oxalic acid in 50% alcohol solution gives a delicate test for sodium, but no rapid method was found of removing the interfering potassium, without introducing free acid which prevents the precipitation of the acid sodium oxalate.

Potassium fluozirconate in 50% alcohol solution, is a delicate reagent for sodium, but potassium solutions also precipitate it.

Tartaric acid in 50% alcohol solution does not completely precipitate the potassium in potassium chloride because of the free mineral acid that is simultaneously formed, hence tartaric acid cannot be used in place of the fluoboric acid.

The advantages of this new method are:

1. Tests may be made in the presence of magnesium, the removal of which, generally a long difficult task, is necessary if the potassium pyro-antimonate method is to be used.

2. The reagents are comparatively cheap and are very easy to prepare.

3. The reactions and equations are simple and easily understood, and only a short time is required to make an analysis.

4. The test is decisive, and the student has confidence in his work. A large class of inexperienced students obtained very accurate results in a trial of the method lasting two terms.

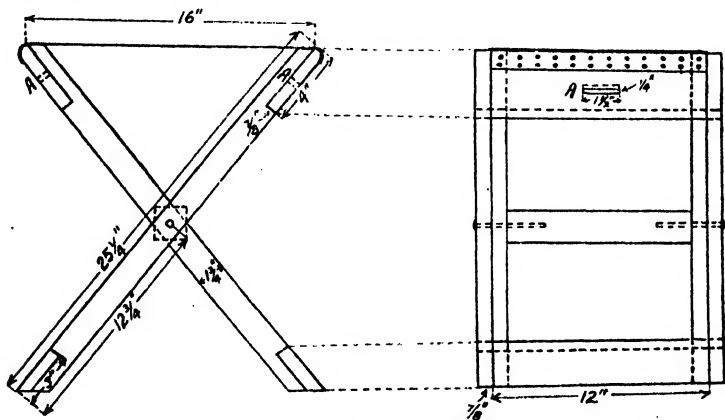
INDIANA UNIVERSITY, BLOOMINGTON.

¹ Mathers and Lee, *Indiana Univ. Studies*, 9, 180 (1912).

NOTES.

A Laboratory Stool.—The laboratory stool pictured herewith is an ordinary camp stool of strong construction, so made as to serve as a device for locking the drawers and doors of the student's compartment. For a laboratory table 33 inches high the dimensions shown on the sketch will be found convenient.

Two holes, A, A, are so placed as to fall together when the stool is closed. A large staple is attached to the wooden strip that separates the drawer from the locker-doors of the ordinary laboratory table. At the end of the laboratory period the student closes his stool, hangs it under the edge of his table, the staple being passed through the holes A, A, in the stool, and snaps a padlock on the outside. It is then impossible to open the locker, since both drawers and locker-doors are blocked by the stool. A single padlock is thus made to do service for from two to four locks.



The stool can easily be carried about the laboratory to suit the convenience of the student, or may even be taken into another room, but must be returned to its place beneath the edge of the laboratory desk before its owner will be able to lock his compartment. If each stool be numbered on both sides with a number corresponding to the locker to which it belongs, there will be little temptation for the lazy student to take his neighbor's stool when he is ready to lock his desk and leave the laboratory.

If one end of the laboratory be provided with a blackboard, and the nearest desk raised six inches above the level of the others, it will be possible for the students in a fairly large laboratory to get near enough to permit lectures being given there, if movable stools of this kind be provided. Of course if this be done it will be necessary to dispense with the shelving and other superstructure commonly found on laboratory tables, in order that the view may not be obstructed. As a matter of fact the student's reagent-bottles should not be kept on shelves, but in a small tray that may

be put inside his desk; for in this way the reagents are kept cleaner, and the work of the janitor is made much easier.

HORACE GROVE DEMING.

LOS BAÑOS, P. I.

Note on a New Analytical Suction Filter.—The description of the following apparatus which I have invented is not of particular interest simply because it contains certain new features, or even old features combined in a new way, but because it is an apparatus whose value can be measured by its usefulness.

Probably every chemist at some time in his course of study has done a certain amount of quantitative analysis, and in the analysis of more complicated substances, such as dolomite or talc, has felt a desire that he might use a Gooch crucible and a suction filter, in one of the first stages of analysis, owing perhaps to the quickness of the filtration and the simplification by eliminating the necessity of burning the filter paper and many other details which tend to lengthen and make tedious some of these analyses. But the style of the present suction filter makes its use at this stage practically prohibitive, because the next stage of analysis could not be carried on in this vessel, nor could the contents be readily taken out, owing to the awkwardness of its shape.

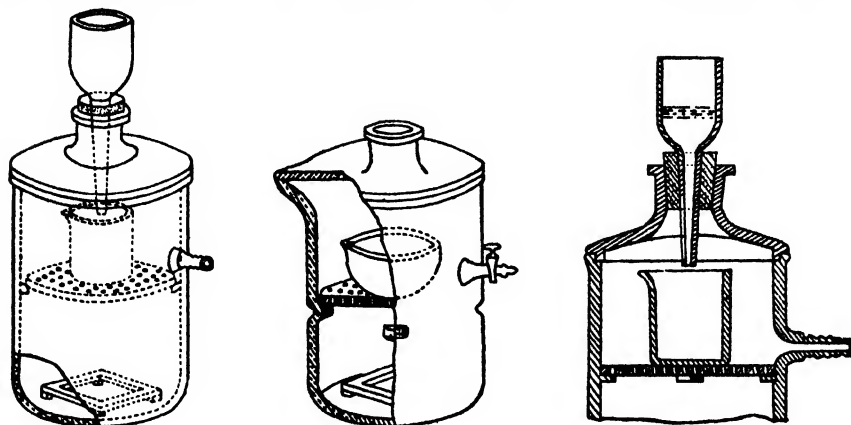
It is often necessary to operate with very small quantities of liquid and it is important in such cases to avoid possible loss of liquid through adherence to the surface of the receptacles employed in making the analysis. At the same time it is desirable to avoid the necessity of carrying in stock various sizes of filter apparatus. It is also necessary to employ for filtering purposes an apparatus which can be easily and conveniently handled and cleansed. It is exceedingly desirable to employ apparatus so constructed as to utilize suction action in effecting the filtering.

So it is the purpose of my filter to provide an apparatus which accomplishes these various desirable results. A description of the apparatus is as follows:

The apparatus is very simple and consists of three parts. The main body of the apparatus somewhat resembles Witts filter, and consists of a cylindrical glass jar, $6\frac{1}{2}$ inches deep and $5\frac{1}{2}$ inches in diameter, with a suction outlet near the top fitted with a ground glass stopcock. The top rim has a pouring lip in the side opposite the suction outlet and the entire upper surface is ground. Half way up from the bottom on the inside surface are three glass protrusions at equal distances apart for supporting a perforated shelf, which is the second part. The third part is the cover having a ground glass rim to fit the upper surface of the jar and having an extra large stopper opening of one and three-quarter inches in diameter.

Now, where small quantities are to be filtered, the shelf is inserted and

a small beaker or crucible is placed thereon to catch the filtrate. After the filtration, whether with a Gooch or ordinary filter, we find the filtrate is in the desired vessel ready for the next operation. If large quantities



are to be filtered the shelf is removed and a large beaker inserted; or the jar itself may be used very conveniently, the three small protrusions interfering but little in washing, and the pouring lip facilitating the emptying of the jar.

There are, indeed, many suction filters which in certain respects resemble my filter, but owing to their lacking in certain features have not rendered themselves very popular. My filter I find the most simple and natural, and at the same time most convenient for speed, neatness and accuracy, and for that reason have called attention to it and have named it the Takamine Analytical Filter (for which the patent is pending).

JOKICHI TAKAMINE, JR.

NEW YORK.

An Alternating Current Thermoregulator.—The electromagnetic thermostat regulator is a well-known convenient instrument. The principle of operation is that the expansion or contraction of mercury in a large open mercury thermometer makes or breaks a contact which throws on or off a current through an electromagnet.

Regarding these regulators Ostwald¹ says: "The great drawback I find with such instruments is that the current always remains closed for a considerable length of time. This causes a rapid running down of the battery which in turn easily occasions the regulator to fail in its action."

It was suggested by Professor J. W. Dorsey of the electrical engineering department of the University of Manitoba that alternating current from the city mains might be used to run the electromagnet and accordingly

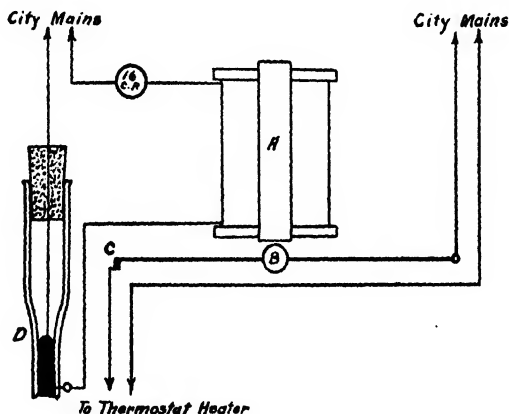
¹ "Physico Chemical Measurements," 1894, p. 62.

an arrangement was constructed as shown in the diagram. It may be a surprise to many chemists to know that an electromagnet can be run by alternating current, but with a current of 60 cycles the pull on the armature is quite appreciable.

The electromagnet had the following construction: The soft iron coil A was 4.5 cm. long and 0.9 cm. in diameter.

The winding consisted of about 350 turns of No. 20 insulated copper wire wound directly on the coil and well protected at the ends by two hard rubber disks.

The soft iron armature B was sawed from a circular bar. It was 0.8 cm. in diameter and 0.2 cm. thick. It was soldered to a piece of No. 19 copper wire as shown in the diagram. The position shown there was chosen



for the armature because then only a small surface came in contact with the core and also the pull of the electromagnet seemed to be stronger than in any other position of the armature.

The electromagnet and lamp resistance were fastened permanently on the wall beside the thermostat in such a position that when no current is flowing through the electromagnet the armature falls down and the circuit through the thermostat heater is completed at C. An excessive temperature in the thermostat causes the mercury in the regulator to rise and completes the other circuit at D. The electromagnet then draws up and retains the armature, breaking the heating circuit at C. The wires at C must be fairly stout to prevent overheating and sticking due to sparking. The vibration of the armature also tends to prevent sticking of the contacts.

The amount of electric power used in the electromagnet coil and in the lamp resistance is small. This apparatus has been in use for two months and has given satisfaction.

HAROLD S. DAVIS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

A STUDY OF THE REACTIONS OF SODIUM MALONIC ESTER.¹

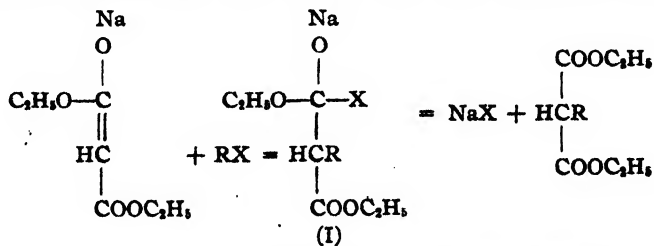
[FIRST PAPER.]

By C. LORING JACKSON AND F. C. WHITMORE.

Received March 17, 1915.

This paper contains a proof that the first step in the reaction of sodium malonic ester and an organic halogen derivative consists in the union of the two reagents to form an addition compound. It therefore places on a firm experimental basis that part of the theory proposed recently by Bigelow and one of us to explain these reactions; but it has also a wider interest, since it increases by one the meagre list of such intermediate compounds, and thus adds weight to the common theory that substitution is preceded by addition.

In 1888 W. S. Robinson and one of us² found that when sodium malonic ester reacted with tribromodinitrobenzene one of the atoms of bromine was replaced by hydrogen and one by the malonic ester residue, while the third remained unaltered, giving bromodinitrophenylmalonic ester. Further work in this laboratory led to the discovery of other cases of this strange replacement of a halogen by hydrogen, but no progress was made toward explaining the reaction until 1911, when H. E. Bigelow and one of us³ found that bromotriiododinitrobenzene was converted by sodium malonic ester in the cold into bromodiiododinitrobenzene, but, if the reagents were heated, that bromoiododinitrophenylmalonic ester was formed. These experiments showed that the replacement of halogen by hydrogen preceded that by the malonic ester radical, and led to the following explanation³ of the reactions with sodium malonic ester: When an organic substance containing a halogen reacts with sodium malonic ester, the first step consists in the addition of the halogen and the organic radical to the (enol) sodium malonic ester. Owing to the attraction of the sodium, the more negative part of the compound will be added to the carbon atom carrying the NaO. As a rule this would be the halogen

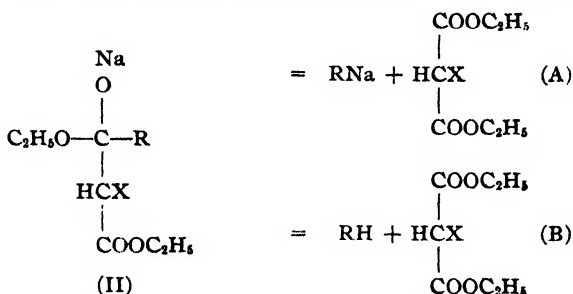


¹ The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Frank Clifford Whitmore.

² *Am. Chem. J.*, **11**, 93 (1889).

³ *Ibid.*, **46**, 549 (1911).

(X), and the addition compound would have Formula I, which then would easily lose sodium halide forming the substituted malonic ester. There are exceptional cases, however, in which the organic radical (R) is more negative than the halogen (X), especially if this is bromine, or, better still, iodine, then the addition compound will have Formula II and can



break up in two different ways. If the radical can combine with sodium, this salt will be easily formed with halogen malonic ester as the secondary product (A). If it cannot combine with sodium, the addition compound should be much more stable than in the two preceding cases, but on acidification the hydrogen compound of the radical will be formed, leaving halogen malonic ester (B).

This theory also applies to other esters, which can form enol sodium salts like acetoacetic ester, or camphocarboxylic ester. It will be more convenient to postpone to a second paper the discussion of the apparently similar reactions, which are obtained with sodium alcoholates. It should be borne in mind that the course of most reactions is influenced by several conditions. All that we claim is that the condition stated in our theory is always important and often controls the course of the action.

The idea that the formation of an addition compound is the first stage of the sodium malonic ester reactions is not new, as it was first published by Michael¹ in 1888, and in a somewhat different form by Nef² in 1891. In 1905 Michael³ tried to isolate one of the addition compounds, but his results have been questioned.⁴ The original part of this theory is the idea that the sodium exercises a directing influence on the manner of the addition, but, after this had been published,⁵ a more careful study of the literature showed that it also had been anticipated by von Findeisen⁶ to explain his results from the action of tolylsulfochloride on sodium acetoacetic ester—results which had already been obtained by Kohler and Mac-

¹ *J. prakt. Chem.*, **37**, 487 (1888).

² *Ann.*, **266**, 59 (1891). Compare also Michael, *J. prakt. Chem.*, **46**, 190 (1892).

³ *Ber.*, **38**, 3217 (1905).

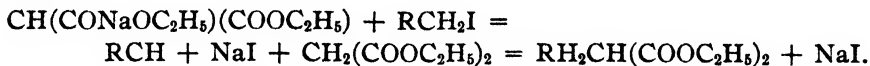
⁴ Paal, *Ber.*, **39**, 1436, 2859 (1906); **41**, 58 (1908); **42**, 277 (1909).

⁵ Jackson Bigelow, *Am. Chem. J.*, **46**, 549 (1911).

⁶ *J. prakt. Chem.*, **65**, 530 (1902).

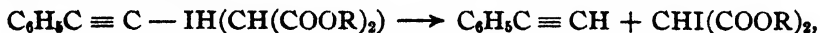
Donald.¹ Von Findeisen, however, did not attempt to make a more general application of the theory, or to test it by further experiment.

We have found only two different explanations of the reactions of sodium malonic ester, both of which were advanced by Nef. The first² explains the usual reactions by supposing that the alkyl halide dissociates into the halogen acid and a methylene compound, to which malonic ester is then added.



It seems to us that a fatal objection to this theory is found in the fact that it does not explain such reactions as the formation of benzoylmalonic ester from benzoylchloride, or the conversion of trichlorotrinitrobenzene into dichlorotrinitrophenylacetic ester³ (a product of the decomposition of the original malonic ester).

Nef's second theory⁴ deals with the less usual reactions, in which hydrogen takes the place of a halogen. Here he assumes an addition of malonic ester to the halogen,



and that the addition compound at once falls into the hydrogen derivative and the substituted malonic ester.

Among the objections to this theory, which have occurred to us, the following seem of especial weight: The work described in this paper shows that the addition compound is not made up of *free* malonic ester and the other reagent, as maintained by Nef, but contains sodium; and while such a product might be expected with iodine because of the analogy between $\text{K} - \text{I} = \text{I}_2$ and Nef's compound, $\text{Na} - \text{I} = (\text{CH}(\text{COOR})_2)\text{R}'$ (in which R' is a negative radical), it is much less likely that it would be formed with bromine, for which we can find little analogy; and what we know of chlorine makes it very improbable that such a compound could be derived from it. In fact Nef emphasizes this point to explain the difference in behavior of the bromo and iodophenylacetylenes on one side and the chloro compound on the other. Later, however, Willcox,⁵ in a paper from Nef's laboratory, showed that the behavior of the ethylsulfuric chloride made it necessary to extend the theory to the chlorine compounds in the face of this acknowledged objection.

¹ *Am. Chem. J.*, 22, 228 (1899).

² *Ann.*, 298, 263 (1897).

³ Jackson and Smith, *Am. Chem. J.*, 32, 174 (1904).

⁴ *Ann.*, 308, 306 (1899). In this paper he says that C. L. Jackson and his scholars have never detected the ethanetetra-carboxylic ester as the other product of these reactions. This is a mistake, as its presence was reported in 1890, Jackson and Moore, *Am. Chem. J.*, 12, 7, and Jackson and Dunlap, *Ibid.*, 18, 117 (1896), while tartronic acid was detected even earlier, Jackson and Robinson, *Ibid.*, 11, 541 (1889).

⁵ *Am. Chem. J.*, 32, 449 (1904).

Nef's addition compound contains the halogen already combined with sodium, and his theory assumes that in decomposing the halogen breaks away from the sodium to combine with the carbon of the malonic ester, but certainly such a startling hypothesis cannot be accepted, until it has been supported by most convincing evidence.

According to Nef's theories the formation of substituted malonic esters and the replacement of halogen by hydrogen are brought about in entirely different ways, so, for instance, to explain the formation of bromotrinityphenylmalonic ester from tribromotrinitybenzene¹ one of the atoms of bromine must have taken up sodium and the malonic ester residue, and another have been split off as hydrobromic acid, if this were possible, but no reason is given to explain why these two atoms of bromine should react entirely differently. Until these objections are removed, it seems to us that our theory should be preferred to those of Nef, as it explains all these observations in a satisfactory manner, as will be shown in our second paper.

In continuing the study of our theory we have tried to submit it to the test of experiment in two ways: First, by isolating the addition compound predicted by it, with results described in this paper; and, second, by studying the effect on the course of reaction of the relative attraction for sodium of the two radicals added, which will be described in a second paper.

Before discussing our quantitative experiments on the addition compound the proofs of its formation may be given. When the pale yellow bromotriiododinitrobenzene is treated with colorless sodium malonic ester in the cold, the mixture turns dark blood red, and if this solution is acidified, the color is discharged, owing to the formation of bromodiododinitrobenzene and ethanetetra-carboxylic ester (or iodomalonic ester), which are colorless, or nearly so. These changes of color, therefore, can be due only to the formation and destruction of a new compound under the conditions predicted by our theory; and the only compounds we can find, which could be formed under these conditions, are our addition compound, or one of the strongly colored salts of a quinol nitro acid;² but the latter substance on acidification would give the original triiodo-compound, and certainly could not form the iodomalonic ester and bromodiododinitrobenzene actually obtained, so this alternative must be rejected, and there is left as the only cause of this red color the formation of the addition compound required by our theory. The similar observations when 1,3,5-triiododinitrobenzene was treated with sodium malonic ester³ furnishes us with another undoubted case of a colored addition

¹ Jackson and Moore, *Am. Chem. J.*, 12, 7 (1890).

² Jackson and Gazzolo, *Ibid.*, 23, 376 (1900).

³ Jackson and Langmaid, *Ibid.*, 32, 297 (1904).

compound; and we may have observed many others, as a marked change of color was observed in every one of the 83 reactions studied in this laboratory, in which a nitrohalogen aromatic compound was treated with sodium malonic ester, sodium acetacetic ester, or a sodium alcoholate, but, although some of these colors may have been caused by one of our addition compounds, we can prove this to be the case only in the two reactions already given, as in each of the others it was possible a quinol nitro salt was formed and frequently also a colored salt of one of the reaction products.

The second proof of the formation of our addition compound is furnished by its solubility, as 10 cc. of absolute alcohol dissolve over 10 g. of the red product, but only 1.5 g. of sodium malonic ester and 0.043 g. of bromotriiododinitrobenzene, so there was in solution more than 6 times the weight of solid, which would have been dissolved, if there had been only a mixture of the two components.

This red compound made from bromotriiododinitrobenzene and sodium malonic ester is particularly well adapted for study, because it is very stable, keeping unaltered for nearly a year, is formed almost quantitatively, and the main reaction is not embarrassed by parallel or subsequent reactions. Most of the other addition compounds we have considered are inferior to this in at least one, or, sometimes in all three, of these respects.

After preliminary experiments had established the comparative stability of this compound in the cold, and had shown that it could be obtained from its solutions only by evaporation, we were confronted with the problem of determining the composition of a very soluble amorphous substance, for, although in one experiment we had obtained crystals, which seemed to be the addition compound, in a year and a half of attempts to prepare them again, we never observed the least sign of crystallization. Owing to the difficulty in purifying such a substance, we first made a set of analyses of specimens containing the addition compound mixed with a known quantity of one or the other reagent.

As the bromotriiododinitrobenzene is only slightly soluble in absolute alcohol, preparations were made with a sufficient excess of this reagent to saturate the alcohol used, and leave a small quantity of the solid. After the reaction with sodium malonic ester had taken place, the solution was filtered off, a portion evaporated *in vacuo* (it decomposed, if warmed), and the amount of sodium in the residue determined. The weight of bromotriiododinitrobenzene which dissolved in the volume of alcohol used, was determined by a parallel experiment, and on subtracting this from the weight of the residue there was left the weight of the addition compound containing the sodium. Possible weak points in this method of attack were that the reaction might not run to an end, and that the presence of the addition compound might change the solubility of

the substituted benzene. The first of these difficulties evidently did not exist, however, since the percentages of sodium agreed within 0.2% with that calculated for $(C_6BrI_3(NO_2)_2)(CH(CONaOC_2H_5)(COOC_2H_5))$, and the absence of the second was proved by the fact that solutions containing much of the addition compound gave the same analytical results as the more dilute, which would have been impossible, if the size of the correction had been affected by the presence of this substance. Similar experiments were tried with a known excess of sodium malonic ester, the solvent being a mixture of benzene and alcohol, which takes up but little of this substance. Applying the correction in this case for the amount of sodium malonic ester dissolved, the percentage of halogens in the residues differed from that calculated for the addition compound by only 1.25% in the worst case. Here, again, the agreement is better than we expected, as this correction would be seriously affected by the moisture and carbon dioxide of the air forming malonic ester, which would add to the weight of the substance analyzed. Exposure to the air was avoided as completely as possible, and evidently with good success, as the error is little, if at all, greater than would be expected from the larger size of the correction than in the preceding case.

These determinations do not *prove* the existence of the addition compound, as they were made with unpurified residues, which did not crystallize or show any other criterion of their freedom from impurities beside the known excess of one of the reagents, but they certainly furnish a strong argument in favor of its existence, as the first series proves that a given volume of alcohol in presence of sodium malonic ester takes up more bromotriiododinitrobenzene than it can alone, and this additional amount dissolved is just sufficient to form a compound made up of one molecule of each reagent. This amount is considerable, for instance in one determination the alcohol, which would normally have taken up only 0.0622 g., with the sodium malonic ester dissolved 0.2397 g. In the second series the bromotriiododinitrobenzene caused the benzene and alcohol to dissolve an amount of sodium malonic ester in addition to that, which would be taken up by the solvent alone, exactly enough to form this same compound.

We tried next to obtain a pure specimen of the red addition compound, using the constituents in molecular proportions in a mixture of benzene and absolute alcohol. The resulting solution, after it had stood several days, was evaporated *in vacuo* till sufficient solid had deposited, and, after this had been filtered out, a second solid red fraction was obtained from the filtrate, but the filtrate from this yielded a dark red liquid. Analyses showed that the least soluble fraction contained bromotriiododinitrobenzene, the most soluble fraction malonic ester, or its sodium salt, while the intermediate fraction gave a percentage of halogens agree-

ing with that for the addition compound. These experiments therefore showed that the substance could be purified by this fractional evaporation. It is to be observed that with equal molecules of the two reagents the action does not run to an end, whereas our previous series of experiments indicated that with a large excess of one of the reagents the other was completely used up.

The way had now been cleared for the study of the homogeneity of the addition compound. A large amount of it was made, as in the second series of experiments, and submitted to an elaborate systematic fractionation, in which 29 solid fractions were obtained. This work was tedious in the extreme, as it was necessary to carry on all the evaporations at ordinary temperatures. Analyses of the most and least soluble fractions showed that the unaltered portions of the two reagents accumulated in these as in the second series, and, after these had been rejected, a considerable amount of intermediate material was left, which was divided into 4 fractions according to solubility, when analyses showed that the percentage of halogens in the least soluble fraction agreed absolutely with that in the most soluble. It seems to us that this proves the red addition product is a definite compound with the composition



We also describe in this paper some improvements in the preparation of triiodoaniline, which make it possible to obtain this substance in a state of purity with tolerable certainty.

Experimental.

Preparation of Triiodoaniline (Monochloride of Iodine).—Success in this preparation depends in great measure on the purity of the monochloride of iodine used, since a slight excess of free iodine, or, worse still, of trichloride of iodine, gives a black product, which produces distressing results, when submitted to the diazo reaction. Our predecessors tried to avoid this difficulty by continuing the action of the chlorine on the iodine until a few yellow crystals of the trichloride appeared, when the attempt was made to remove this impurity either by heat or the addition of iodine.¹ These methods proved unsatisfactory, partly because the amount of impurity was considerable, since much of the trichloride was needed to saturate the monochloride, before the crystals appeared, and partly because the action of heat in removing it was incomplete without too great a loss of the monochloride, or the action of iodine on the trichloride was exceedingly sluggish. We have accordingly substituted for them a process, in which the monochloride is prepared with little more than a trace of free iodine, and the temperature, at which it is driven over into the aniline hydrochloride, is kept so low that most of this iodine is left

¹ *Am. Chem. J.*, 26, 55 (1901); 46, 557 (1911).

behind. Our process is based on Stortenbeker's¹ work on the equilibria in the system iodine-chlorine. Out of 12 preparations we obtained with it white, or nearly white, triiodoaniline in 11, the twelfth being only pale brown, whereas a white product was the exception rather than the rule with the older processes.

A rapid stream of chlorine, dried by several spiral washing tubes of strong sulfuric acid, was passed over 42 g. of cold iodine (the amount for 10 g. of aniline) in a flask. The point at which the process should be stopped was determined by watching carefully the appearance of the product after all the crystals of iodine had disappeared. If some of the liquid was shaken up on the side of the flask at this point, it left a sticky opaque coating, but, as more chlorine was added with constant shaking, the liquid flowed from the side of the flask without wetting it; which in turn was followed by a more perfect liquefaction, so that the side of the flask was wet once more, leaving a slightly streaked layer red and transparent, when held to an electric light. The action of the chlorine was stopped when this streakiness had almost, but not quite, disappeared. It seemed to be caused by free iodine, which in this way was reduced to a minimum with no danger of forming any of the much more injurious trichloride of iodine. If the action of the chlorine was carried too far, the red transparent film on the side of the flask was entirely uniform. Such a preparation solidified on cooling to a mass of long, dark red needles, but gave an impure triiodoaniline as the rapid crystallization was brought about by a little trichloride of iodine. A specimen prepared by stopping the chlorine at the right point did not solidify even after standing for several days at 0°, probably because the slight excess of iodine prevented the crystallization. This was left behind in the flask, after the monochloride had been drawn over into the solution of aniline hydrochloride.

To prepare the triiodoaniline 10 g. of freshly distilled aniline were dissolved in 1 liter of strong hydrochloric acid, twice the quantity used by our predecessors, which, although it slightly lowered the yield, gave a purer product. The solution was then diluted to 7-8 liters and a rapid stream of air sucked through it, which had previously passed through the weighed flask containing the monochloride of iodine heated to 20-30° in a water bath. This very low temperature reduced any decomposition of the monochloride to a minimum, and also kept back most of the free iodine. After the calculated amount of the monochloride had volatilized, the solution with the flocculent precipitate was allowed to stand over night, filtered through a large cloth bag, as suction rendered the precipitate unmanageable, washed free from hydrochloric acid, and dried on a steam radiator. The yield of crude triiodoaniline amounted in 11 experiments to 480 g. from 568 g. of the monochloride of iodine, that is 85% of the

¹ *Z. physik. Chem.*, 3, 11.

theory. The products varied from light gray melting $165-172^{\circ}$ (uncorr.) to pure white melting as high as 178° (uncorr.). Pure triiodoaniline melts at 185.5° . If the monochloride of iodine was a bad preparation, or the triiodoaniline was black, it saved time to throw it away, rather than to try to get a pure substance from it.

The crude triiodoaniline was extracted several times with small quantities of boiling alcohol, which left a residue of the pure substance melting at 185° (uncorr.) instead of 185.5° . The first of these alcoholic extracts were very dark, even when the crude triiodoaniline was nearly white. From them two substances were obtained. The first by cooling the mother liquors from a specially impure triiodoaniline, after they had been evaporated to small volume. The substance thus obtained proved after several recrystallizations from alcohol to have the constant melting point 95° (uncorr.), and is therefore diiodoaniline, which melts according to Rudolph and Michael and Norton¹ at $95-96^{\circ}$. This inference was confirmed by the analysis of a slightly impure specimen.

Diiodoaniline Hydrochloride.—The second compound was obtained in quantity from a specimen of the triiodoaniline, which had been dried without washing it free from hydrochloric acid, but small amounts of this and the free diiodoaniline were formed in every preparation of triiodoaniline. The alcoholic extract from the specimen first mentioned deposited it in silvery white plates melting near 200° . As it was found impossible to purify it by crystallization, which, on the contrary, rendered it more impure, the original crystals were dried *in vacuo* and analyzed I. Another sample was made by dissolving diiodoaniline in dry benzene and treating it with dry hydrochloric acid gas. The white precipitate was dried *in vacuo*. II.

I, Subst. 0.1854, II, 0.2286, 2090; $\text{AgCl} + \text{AgI}$, 0.2973, 0.3676, 0.3379. Calculated for $\text{C}_6\text{H}_4\text{I}_2\text{NH}_2\text{HCl}$: Cl + I, 75.88; found: 75.73, 75.95, 76.37.

The two preparations showed the same properties. Silver white plates blackening slightly at 185° and melting with decomposition at 207° (uncorr.). Water does not act on it in the cold but when hot decomposes it into diiodoaniline and hydrochloric acid, as would be expected from the fact that the triiodoaniline hydrochloride has not been prepared.

Preparation of Bromotriiododinitrobenzene.—Ten grams of the triiodoaniline prepared and purified as described above were mixed in a heavy walled Erlenmeyer flask with 120 cc. of glacial acetic acid and 50 cc. of fuming hydrobromic acid, and 3 g. of powdered sodium nitrite added so slowly that an entire day was occupied by the addition, the flasks being kept stoppered during the reaction, which seemed to succeed better under this slight pressure. After standing over night the diazo compound was decomposed by warming, and the solid product extracted

¹ Ber., 11, 78, 109 (1878).

with small quantities of alcohol, till the residue melted at 142° (instead of 146°). It was found not worth while to use the crystals obtained from the extracts. This process differs in several particulars from that given by Bigelow and one of us,¹ the most important being the use of fuming hydrobromic acid instead of the constant boiling acid. This was obtained by passing hydrobromic acid gas into a constant boiling specimen made from sulfuretted hydrogen, bromine and water. The bromotriiodobenzene was sometimes gray instead of yellow, but gave the dinitro compound without difficulty.

The bromotriiodobenzene melting not below 142° was boiled for 4 hours with nitric acid of sp. gr. 1.51 in a flask fitted to a return condenser by a ground joint, and instead of allowing the mixture to cool the hot acid was decanted from the crystals, which were then washed by decantation with water. These white, feathery crystals always melted above 280° and sometimes at 290° (instead of 292°). The yield was nearly 50%. The hot acid contained only material so impure and in such small amount that it was not worth while to purify it. The improvements introduced by us into these preparations remove the necessity of the tedious crystallizations, which were a feature of the earlier work.

The Addition Product of Bromotriiododinitrobenzene and Sodium Malonic Ester.—When these two substances are mixed in absolute alcohol, or benzene solution, a dark blood-red color appears, which is destroyed by acidification with the formation of bromodiiododinitrobenzene and ethanetetra-carboxylic ester as the principal products. The red substance formed in this way shows considerable stability, if protected from water and acids. A specimen of the solution made with equal molecules of the components did not lose its color, or form any precipitate even after standing over two years in a sealed tube. In order to test its stability under more exacting conditions we made a preparation in benzene and alcohol with 4 molecules of the ester to one of the benzene compound, as we thought at that time this excess would favor the decomposition of the addition compound, but after standing 3 weeks no test for a sodium halide was obtained in the white precipitate, which had come down, and this was therefore only sodium malonic ester precipitated slowly by the benzene. To meet the objection that sodium iodide might have been formed but retained in colloid solution in the benzene,² the experiment was repeated with exactly the same result in absolute alcohol, where there is little chance of the formation of a colloidal solution. A fuller study led us to believe that varying the proportion of sodium malonic ester from 1 to 5 molecules had no effect upon the reaction, except that an excess made the red color appear sooner in benzene and alcohol, and the bromotriiododinitro-

¹ *Am. Chem. J.*, 46, 549 (1911).

² Compare Paal and Kuhn, *Ber.*, 39, 2859 (1906).

benzene dissolve more rapidly in alcohol, than when the reagents were used in equivalent amounts. Although the red solution was so stable in the cold, it decomposed, when heated for 2 hours, forming a considerable precipitate of sodium iodide whether in alcohol or in alcohol and benzene. It was necessary, therefore, to carry on all the evaporations in our experiments at ordinary temperatures, which greatly increased the tediousness of the work.

In our attempts to isolate the red addition compound we tried first to precipitate it from its benzene solution by the addition of other solvents, but without success, for although ligroin precipitated a red oil, this seemed less manageable than the residues left after evaporating off the benzene; and no other solvent produced any effect, if it was dry and free from acid. As it is a sodium salt we next tried to replace the sodium by some other metal in the hope of getting an insoluble product. For this purpose the red alcoholic solution was treated with silver nitrate, calcium chloride, ferric chloride, or mercuric chloride dissolved in absolute alcohol, but in no case was a precipitate formed.

The negative results of these experiments reduced as to obtaining the substance by evaporation, which was carried on to best advantage in a Hempel *vacuum* desiccator charged with fused potassium hydroxide. With this 175 cc. of a mixed benzene and alcohol solution were reduced to 15 cc. in about 20 hrs. instead of taking 3 days or more, as was the case when a common *vacuum* desiccator with sulfuric acid was used. We tried also passing a stream of air through the liquid from a capillary tube, while a *vacuum* was maintained, as in distillation under diminished pressure, but this worked no more rapidly than the Hempel desiccator, and was more apt to lead to decomposition because of the difficulty in removing all traces of moisture and carbon dioxide from so large a volume of air. The residues at first were red oils, or tars, which, after all the solvent had gone, were converted into amorphous viscous solids of a dark red color. If the process had succeeded, these showed no signs of crystallization; if it had not, white crystals were deposited in small amount, which were either unaltered bromotriiododinitrobenzene, or ethane-tetracarboxylic ester formed by carbon dioxide from the air. Such specimens were rejected. The result was the same, whether the reaction took place in benzene and alcohol, or in absolute alcohol alone.

After working on this substance for half a year one preparation containing a large excess of malonic ester deposited a few minute clusters of crystals, which looked black to the naked eye, but under the microscope appeared as red plates. As they looked not unlike iodine, they were carefully tested for this substance with negative results. They dissolved easily in alcohol with a red color, and kept between two sealed watch glasses apparently unaltered for nearly a year, after which they became

tarry. The quantity was too small for decisive study, but the appearance and properties justify the surmise that they were crystals of the addition compound. For a year and a half we tried by every modification of the process we could devise to get such crystals again, but have not even caught a glimpse of them. Substituting malonic methyl ester for the ethyl compound gave no better result in spite of the greater tendency of methyl compounds to crystallize.

Sodium Determinations Made with the Impure Addition Compound.—As at first there seemed little chance of obtaining a pure specimen of the addition compound, we determined the amount of sodium in a preparation containing a known amount of the bromotriiododinitrobenzene. The results were even better than we had hoped.

The specimens were prepared in absolute alcohol, in which the red product is very soluble, whereas a series of determinations showed that 100 cc. of absolute alcohol dissolve of the bromotriiododinitrobenzene only 0.416 g. at 15°, 0.420 g. at 16°, 0.432 g. at 20°, and 0.440 g. at 21°. We proceeded as follows:

The clean sodium was weighed to milligrams in a weighing bottle under kerosene oil, and after drying quickly with filter paper was dropped into absolute alcohol, which, like all used in this work, had been distilled after treatment with a little sodium to remove the last trace of water. The malonic ester corresponding to the sodium was then weighed to centigrams, and also an amount of bromotriiododinitrobenzene, which gave one molecule of this substance for each molecule of the ester, and an excess more than enough to form a saturated solution with the amount of absolute alcohol used. The substituted benzene was first boiled with absolute alcohol, which dissolved only a small part of it, and after it had been cooled, the malonic ester was added, and finally the cool sodium ethylate solution. A dark red color appeared instantly, and after 5 minutes most of the solid had gone into solution. The flask was allowed to stand at about 20° for 2 or 3 days with occasional shaking to complete the reaction. Another flask was prepared with portions of the same specimens of bromotriiododinitrobenzene and absolute alcohol, and exposed to exactly the same conditions to determine the amount dissolved. At first very dilute solutions of the red compound were used, so that its presence might not change the solubility of the bromotriiododinitrobenzene. Later, stronger solutions were used, in which the correction for the dissolved bromine compound was much smaller in proportion to the amount of red product. As the two sets of corrected results agree with each other, the method of correcting for the presence of the dissolved benzene compound must be at least approximately accurate.

After the two flasks had stood for at least 3 days, the temperatures were taken, the contents filtered to remove undissolved bromotriiododinitrobenzene, and the filtrates kept in well-stoppered bottles, which as a further precaution were sealed with hard paraffin. 25 cc. of the filtrate were transferred to a platinum crucible and the solvent evaporated in a vacuum desiccator over sulfuric acid and a trace of potassium dichromate, as experiment had shown that evaporation on the steam bath decomposed the red substance. After most of the solvent had evaporated, a fresh portion of 25 cc. of the filtrate was added, and the process continued until a sufficient amount of residue had been obtained. The residue was brought to constant weight *in vacuo*—a very tedious process, as the viscous solid retained traces of the solvent obstinately. It was found later that the work would have gone less slowly with a potassium hydroxide

Hempel desiccator; as it was, the shortest of these determinations lasted 10 days. The weighed product was then treated with a little strong nitric acid and strong sulfuric acid in the cold. This must be done with great caution to avoid spattering, as the decomposition was attended with a vigorous effervescence. The sodium was then determined in the ordinary way. Before calculating the analyses the weight of substance was corrected by subtracting from it the weight of bromotriiododinitrobenzene contained in the same volume of the solvent, which had been submitted to the same conditions in the blank experiment.

Residue, 0.3725, 1.6648, 2.4136. Correction, 0.0622, 0.4662, 0.5080. Subst., 0.3103, 1.1986, 1.9056; Na_2SO_4 , 0.0284, 0.1016, 0.1653. Calculated for $\text{C}_6\text{BrI}_3(\text{NO}_2)_2\text{CHCO-NaOC}_2\text{H}_5\text{COOC}_2\text{H}_5$: Na, 2.85; found: 2.96, 2.75, 2.81.

The results agree with each other and with the theory better than we had expected.

Determinations of Halogens in the Impure Addition Compound.—In these analyses the quantity of sodium malonic ester used was so large that some of it remained undissolved in the solvent consisting of 1 part absolute alcohol to 12 of benzene (dried with sodium). The correction to be applied for the dissolved sodium malonic ester was determined by a parallel blank experiment in each case. In all other respects the procedure was the same as in the determinations of sodium. The halogen determinations were made by the method of Carius in a portion of the residue dried *in vacuo* to constant weight.

Residue, 0.3148, 0.3398, 0.3279. Correction, 0.1205, 0.1300, 0.1255. Subst., 0.1943, 0.2098, 0.2024; $\text{AgI} + \text{AgBr}$, 0.2191, 0.2368, 0.2248. Calc. for $\text{C}_6\text{BrI}_3(\text{NO}_2)_2\text{CHCO-NaOC}_2\text{H}_5\text{COOC}_2\text{H}_5$: I + Br, 57.08; found: 58.20, 58.34, 57.34.

The agreement here, although not so good as with the sodium, is as close as could be expected, when it is remembered that the correction may be seriously interfered with by the moisture and carbon dioxide of the air converting sodium malonic ester into the soluble free ester.

Fractionation of the Addition Compound.—To determine whether the red product was a compound or a mixture, and to obtain it, if possible, free from impurities, specimens of it were next divided into fractions according to solubility. Our first experiments aimed at preparing only 3 fractions. 3.86 g. of malonic ester and 15.1 g. of bromotriiododinitrobenzene (these are not far from molecular proportions) with 0.55 g. of sodium were allowed to react in a mixture of alcohol and benzene for at least 3 days, after which 175 cc. of the solution were evaporated in a Hempel *vacuum* desiccator charged with potassium hydroxide until its volume had been reduced to 10 cc. At this point sufficient solid had been deposited to render the liquid thick, and it was filtered. To secure the filtration of this viscous mass without decomposition by the carbon dioxide, or water in the air, the last part of the evaporation was carried on in a small Erlenmeyer flask, the neck of which fitted the platinum Gooch crucible to be used for the filtration. The hardened filter paper was carefully

fitted to the crucible, and the filtrate was received in a small test tube within the suction flask, which should not be too large. When the substance was ready for filtration, the Erlenmeyer flask was removed from the desiccator, stoppered, and fitted with a thin rubber hose on its neck; the stopper was then replaced by the inverted Gooch crucible with its suction flask, the adjustments being made as rapidly as possible. The suction was started, the apparatus inverted, and the filtration begun. It was found that even a good water pump did not give pressure enough to filter this viscous mass, so a powerful cylinder pump was used, but even with this the filtration lasted several hours. Fortunately, the dark red amorphous solid was not viscous enough to clog the filter. If the process had succeeded, the solid was completely soluble in a very small quantity of absolute alcohol. In some cases, however, it left a slight white residue of bromotriiododinitrobenzene. Specimens of these least soluble fractions from different preparations are numbered I and II in the analyses.

During the filtration the low pressure caused the evaporation of part of the filtrate, so that a second filtration gave a solid like the first, except that it showed a somewhat deeper red color. Specimens of such intermediate fractions are numbered III, IV, V in the analyses. When we tried to secure a third fraction in this way, very little solid was deposited, but we obtained a deep red liquid, which showed no sign of solidification on standing *in vacuo*, or by cooling with a freezing mixture. It was odorless, and mixed easily with benzene or alcohol. Analyses of such most soluble fractions are numbered VI and VII.

| | I. | II. | III. | IV. | V. | VI. | VII. |
|---|--------|--------|--------|--------|--------|--------|--------|
| Subs | 0.2545 | 0.2451 | 0.2273 | 0.3203 | 0.2465 | 0.3070 | 0.3589 |
| AgI + AgBrO..... | 0.2915 | 0.2797 | 0.2532 | 0.3569 | 0.2770 | 0.3225 | 0.3744 |
| Found, I + Br..... | 59.12 | 58.89 | 57.27 | 57.51 | 58.01 | 54.24 | 53.86 |
| Calc. for $C_6BrI_3(NO_2)_2CHCONaOC_6H_5COOC_2H_5$: I + Br, 57.08. | | | | | | | |

A similar experiment with sodium malonic methyl ester gave a least soluble (VIII) and an intermediate fraction (IX).

VIII. Subst., 0.2265, IX, 0.2532 AgI + AgBr, 0.2735, 0.2908. Calc. for $C_6BeI_3(NO_2)_2CHCONaOCH_2COOCH_3$: I + Br, 59.19; found: VIII, 62.33; IX, 59.30.

The intermediate fractions, III, IV, V, and IX, agree sufficiently well with the percentage required by the formula. The less soluble fractions, I, II, VIII, seem to contain a slight impurity of bromotriiododinitrobenzene; the more soluble, VI and VII, one of sodium malonic ester.

A more elaborate fractionation on a larger scale was next undertaken with the object of breaking up the intermediate portion into smaller fractions, the analyses of which would settle the question, whether it was a homogeneous compound, and also, when this work was started, we had not given up the hope of obtaining the red compound in crystals.

A large amount of the red substance was made from equal molecules of the two reagents in a mixture of alcohol and benzene, and after standing 25 days, during which time no solid separated, was evaporated in a Hempel desiccator over potassium hydroxide, and fractionated systematically from absolute alcohol. 29 different fractions were separated—no light task even with the quicker evaporation in the Hempel desiccator, and in this way a large amount of material of intermediate solubility was obtained, which, judging from the results of the previous experiments, should consist of the pure addition compound. This presumably pure material was then divided into 4 fractions, X, XI, XII and XIII, of which the least soluble was X, the most soluble XIII. To show that the impurities had been removed in the preparation of the material for X to XIII, analyses are added of the most impure fractions rejected in making it, the least soluble being XIV, the most soluble XV. XIV and similar very impure least soluble fractions were pale red, and, when treated with absolute alcohol, left a white residue of unchanged bromotriiododinitrobenzene. All the other fractions were dark red and completely soluble in alcohol.

| | X. | XI. | XII. | XIII. | XIV. | XV. |
|---|--------|--------|--------|--------|--------|--------|
| Subst. | 0.2236 | 0.2584 | 0.4532 | 0.3087 | 0.3108 | 0.2322 |
| AgI + AgBr. | 0.2461 | 0.2838 | 0.4968 | 0.3398 | 0.3600 | 0.2407 |
| Found: I + Br. | 56.80 | 56.69 | 56.58 | 56.80 | 59.78 | 53.43 |
| Calc. for $C_6BrI_3(NO_2)_2CHCONaOC_2H_5COOC_2H_5$: I + Br, 57.08. | | | | | | |

It seems to us that the inference to be drawn from the agreement between the analysis of the least soluble fraction X and the most soluble XIII is that the material, from which they were obtained, was a definite compound in a state of purity.

Properties of the Addition Compound, $C_6BrI_3(NO_2)_2CH(CONaOC_2H_5)(COOC_2H_5)$.—It is usually obtained as a very dark red amorphous solid, but on one occasion we think it appeared in clusters of needles so dark red as to look black. The solid can be kept as much as a year, if protected from the air, and its solution showed no sign of alteration after standing in a sealed tube for nearly 2 years. Water or an acid decomposes it, the product, in the latter case, being bromodiododinitrobenzene and iodomalonic ester (or if there is an excess of sodium malonic ester, ethanetetra-carboxylic ester). Heat also decomposes the solution, forming a precipitate of sodium iodide. It is very soluble with a blood-red color in all the common organic solvents except ligroin, which precipitates a red oil from its solution in benzene and alcohol. 10 cc. of absolute alcohol dissolve more than 10 g. of the addition compound, and it seems to be equally soluble in benzene. To give an idea of its remarkable solubility we may say that 15 cc. of a mixture of absolute alcohol with some benzene held in solution 19.5 g. of it, and even when cooled

to -20° deposited no solid except a little benzene. On evaporating further the red solid appeared before the volume had been reduced to 10 cc. No salts containing other metals could be obtained from the addition compound.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE LABORATORY OF THE DODGE & OLCOTT CO.]

AZULENE, A BLUE HYDROCARBON. II.

BY ALFRED E. SHERNDAL.

Received March 24, 1915.

Since the publication of the preliminary notice of the isolation of the remarkable new hydrocarbon which occurs in so many of the essential oils,¹ the following further work has been carried out, and is described below:

- (1) The preparation of a picrate, and its analysis.
- (2) The preparation of artificial blue oils from various oils of the sesquiterpene type.
- (3) The isolation and identification, by means of the picrate, of azulene from the blue sections of the oils of cubebs, camphor, and from the artificial blue gurjun oil.
- (4) The complete reduction of azulene to a colorless dihydrosesquiterpene.

The picrate is readily formed by combining the alcoholic solutions of its constituents, and crystallizes out almost immediately in the form of jet black, shiny needles, melting without decomposition at about 120° , and containing one mol of picric acid to one mol of azulene. This ready formation of a picrate is strong evidence that the hydrocarbon possesses an aromatic structure, since only this class of hydrocarbons has been found to yield additive compounds with picric acid, etc.² No true picrates of the hydroaromatic hydrocarbons have been prepared, the so-called picrates of pinene and thymene,³ being in reality picric acid esters, from which the original hydrocarbons cannot be regenerated. They also differ from the picrates of the aromatic hydrocarbons in conditions of formation, stability, etc. The picrate of azulene, on the other hand, resembles the true additive compounds of picric acid with the aromatic hydrocarbons in ease of formation, decomposition by water or dilute alkalis with regeneration of the original hydrocarbon, melting point, etc. It provides an excellent means of establishing the identity of the blue substances isolated from various oils, and of effecting a final and complete purification of the blue hydrocarbon.

¹ THIS JOURNAL, 37, 167 (1915).

² Bruni, *Chem. Zig.*, 30, 569 (1906); Küster, *Ber.*, 27, 1101 (1894).

³ Lextreit, *Compt. rend.*, 102, 555 (1886); Semmler, "*Die aetherischen Öle*," II, 253.

The method of preparation was as follows: To a solution of 1.0 g. picric acid in 20 cc. 95% alcohol, was added 1.0 g. azulene dissolved in 5 cc. alcohol. In a few minutes the mixture set to a mass of crystals which dissolved again when warmed on the water bath, and on cooling separated out in short, shiny, black needles. These were filtered off on the pump, and dried *in vacuo* over sulfuric acid. Yield, 0.73 g.; m. p. 118°. The picrate dissolves readily in alcohol, acetone and ether with a green color; in benzene and ethyl acetate with a blue color. The green color of the solutions is probably due to partial decomposition in the moist solvents. For the same reason, if dilute alcohol is used in the preparation, a substance with a lower m. p. is obtained, more or less contaminated by oil. Carbon tetrachloride and benzine dissolve out the azulene and leave the picric acid undissolved. To determine the amount of picric acid in the compound, it was decomposed by warm water containing a measured amount of barium hydrate, made up to definite volume, filtered, and the excess of barium hydrate determined by titrating an aliquot portion of the filtrate with standard hydrochloric acid, using phenolphthalein as indicator.

0.445 g. picrate, decomposed by warm water containing 17.6 cc. 0.1 *N* Ba(OH)₂, made up to 100 cc., filtered, and 50 cc. of the filtrate titrated with 0.1 *N* HCl. Required, 3.5 cc.

Found: 54.3% picric acid. Calc. for 1 mol picric acid: 53.5%; for 2 mol: 69.8%; for 1/2 mol: 36.6%.

The picrate accordingly contains one mol picric acid to one of the hydrocarbon.

The method of isolating azulene which was described in the first paper gives at least an approximation of the amount contained in the blue oil. As already shown, an intensely blue fraction which was examined, yielded about 0.28% azulene. Following the same procedure with a dark bluish green fraction of oil of cubebs, the amount of azulene which could be isolated amounted to only 0.03%. This shows strikingly enough how oils containing only a trace of the substance, might be intensely colored and still show the characteristics of a homogeneous substance. To give an idea of the color intensity of azulene, 0.064 g. of the pure hydrocarbon was dissolved in a liter of benzine, and an ammoniacal solution of copper sulfate made up to match it in depth of color. The latter solution contained 0.24 g. CuSO₄ to the liter and matched the azulene solution almost exactly both in depth and shade of the color, showing only a slightly less purple nuance.

The azulene was extracted from the oil of cubebs as follows: 250 g. of the oil were dissolved in 200 cc. of benzine, shaken out thoroughly in a separating funnel with 25 cc. of about 63% H₂SO₄, allowed to settle during a half hour, and the acid solution then drawn off. This was then

diluted with water, and extracted with benzine. The same operation was repeated three times, and the final extraction of the diluted acid made with ether. On evaporation of the ether, a residue of 0.073 g. was left, *i. e.*, 0.03% of the cubebs oil taken. This residue was mixed with a solution of 0.07 g. picric acid in 2 cc. absolute alcohol. The black crystalline mass which soon separated was recrystallized from a little alcohol, yielding then the characteristic black, shiny needles of azulene picrate, m. p. 122°.

The production of blue oils from products which do not originally show any blue color, has already been referred to. Wallach,¹ found that the hydrocarbon obtained by dehydrating guaiol with zinc chloride or phosphorus pentoxide, showed a strong blue color, and ascribed the color to the presence of a small amount of some substance containing oxygen. Gadamer,² in a similar manner, obtained a blue product by dehydrating atractylol, and noted also, that guaieene, by the absorption of oxygen, took on a blue color. α -Gurjunene, when heated under pressure with air or oxygen, yields a blue oil.³ All these colorations are undoubtedly due to the presence of small amounts of azulene, formed from the hydrocarbons by an oxidative process. Another reaction which produces azulene, was suggested in the previous paper, namely the action of sulfuric acid in acetic anhydride. By means of this reaction, blue oils were prepared from the oils of amyris, guaiac-wood, and gurjun, and from the latter azulene was isolated and identified by means of the picrate. The sesquiterpene fraction of oil of eucalyptus also gave a greenish blue oil, while from oil of cedar-wood and caryophyllene of clove oil the distillates showed no trace of blue or green color. The method of procedure was as follows:

10 cc. of gurjun oil were mixed with an equal volume of acetic anhydride and 2 cc. of strong sulfuric acid was added gradually, keeping the flask cool by ice water. A violent reaction took place; the mixture took on an intense purple color which changed to a dark blue, and sulfur dioxide was given off. After standing for some time, steam was passed through the acid mixture, and a distillate of 4 cc. of a dark blue oil was thus obtained. By extracting the azulene from this oil in the usual way, *i. e.*, by dissolving in benzine and extracting with 63% sulfuric acid, a yield of about 0.04% of the gurjun oil taken was obtained. The product gave a picrate which crystallized in coarse, black needles with blunt ends, melting at 122°. The blue oils from guaiac, amyris, and heavy eucalyptus sesquiterpene were made in the same way.

This is far from being a smooth reaction, which is not surprising con-

¹ *Ann.*, 279, 379 (1894).

² *Arch. Pharm.*, 241, 33 (1903).

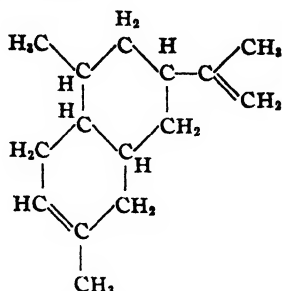
³ *Ber.*, 47, 2252 (1914).

sidering the reagents used, but it shows, as do the other methods of producing blue oils, the nature of the reaction which results in the formation of azulene, namely, a splitting off of hydrogen by oxidative action, which results in the formation of new double bonds. In the terpene series we have the same reaction, that is, the oxidative removal of two hydrogen atoms from the compound $C_{10}H_{16}$, resulting in the formation of cymol, $C_{10}H_{14}$. This also is not a quantitative reaction, the yield of cymol being as a rule very low. But by such means the terpenes are converted into an aromatic molecule, which is structurally closely related to them. Now, all indications point to the conclusion that azulene also is an aromatic hydrocarbon. Its empirical formula, isomeric with the naphthalene homolog $C_{10}H_8 \cdot C_6H_{10}$, its picrate, its high specific gravity, its behavior towards sulfuric acid, are all evidence of aromatic structure. Once this is clear, the striking analogy between the conversion of the terpenes $C_{10}H_{16}$ on the one hand, to the benzene homolog cymol, and on the other hand the conversion of the sesquiterpene $C_{15}H_{24}$ to the aromatic molecule $C_{15}H_{18}$, isomeric with a naphthalene homolog, becomes immediately apparent. The similarity of the reactions by which these conversions are affected adds still more to the analogy. Compare, for instance, the formation of cymol from camphor, with the production of the blue oil from guaïol, both by the action of P_2O_5 ; the formation of cymol from turpentine by heating under pressure with CO_2 , with the formation of a blue oil by heating gurjunene under pressure with air or oxygen; the production of cymol from various terpenes by the action of sulfuric acid, with the formation of azulene by the action of sulfuric acid and acetic anhydride on various sesquiterpenes. The assumption is certainly not far-fetched that an analogous oxidative process takes place in all these cases, which although not smooth, yet from both classes of hydroaromatic compounds, tends to produce aromatic molecules of which the cyclic terpenes and sesquiterpenes, respectively, can be said to be hydro-derivatives. That the nucleus of the azulene molecule is not very different from that of the sesquiterpene from which it is produced, is indicated by the experiment described below, in which its reduction to a colorless dihydrosesquiterpene is effected.

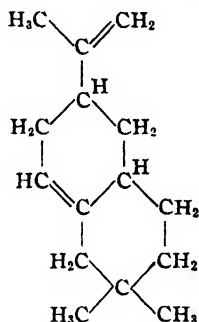
If we could write formulae to illustrate the structure of the various types of sesquiterpenes, it would doubtless help to give an insight into the structure of azulene. The proposed formulae for the sesquiterpenes are, however, based upon such meager experimental evidence, that they cannot be accepted as in the slightest degree conclusive. Some experimental evidence of their close relation to the terpenes and isoprene, was given by Semmler,¹ who succeeded in identifying terpinene in the degradation products formed by heating the gurjunene sesquiterpenes under

¹ *Ber.*, 47, 2252 (1914).

pressure. In general they are assumed to be hydro-naphthalene derivatives. Semmler,¹ in reviewing the possible condensations of three isoprene molecules, brings into consideration, on the basis of unpublished experimental data, the formula



as the type of most of the sesquiterpenes, and states that this type can, under certain conditions, be readily converted into a naphthalene derivative. To another smaller class of sesquiterpenes he ascribes the type formula:



from which no naphthalene derivatives have as yet been obtained. It is evident that in these main types, pinene camphene, or tanacetone rings can take the place of ethylene bonds. The sesquiterpenes also probably include open chain and monocyclic compounds with a corresponding number of double bonds. The number of ethylene bonds, and consequently the ring structure, mono-, bi-, or tricyclic, is determined by the molecular refraction, and in recent times the elegant method of reduction by hydrogen in the presence of finely divided platinum or palladium, has provided an additional means for determining the state of unsaturation, the monocyclic sesquiterpenes being thereby reduced to the saturated molecule $C_{15}H_{30}$, the bicyclic to $C_{15}H_{28}$, the tricyclic to $C_{15}H_{26}$. By this method it was demonstrated that azulene is tricyclic, that is, it contains four double bonds. It was reduced quantitatively to the saturated molecule $C_{15}H_{26}$, which then showed the characteristics of a tricyclic dihydro-sesquiterpene. The reduction was carried out as follows:

¹ Ber., 36, 1038 (1903).

50 cc. of 50% alcohol and 0.2 g. of colloidal palladium were placed in a shaking flask connected with a gas buret, the whole apparatus filled with hydrogen at ordinary pressure, and shaken by a mechanical arrangement till no more hydrogen was absorbed. With a current of hydrogen running through the flask, 2.552 g. of azulene were introduced, the apparatus closed, and the shaking continued until the absorption of hydrogen ceased. The reduction required about twelve hours' shaking, the rate of absorption being uniform throughout and stopping suddenly. At 0°, 760 mm. about 1200 cc. hydrogen were absorbed. Calc. for H_8 : 1146 cc. When the reduction was complete, as shown by the sudden break in the absorption of hydrogen, the mixture was distilled in a current of steam and the oil collected in a narrow graduated tube. In this way were obtained about 2.5 cc. of oil with only a very faint green tint and the following constants:

Sp. gr. at 25°, 0.8935; n_{D20} 1.490, O. R. = 0.

The oil was insoluble in 63% sulfuric acid, gave an intense coloration with acetic anhydride containing a trace of sulfuric acid, and also with bromine in acetic acid solution.

Comparing these constants with those of other tricyclic dihydro-sesquiterpenes, it will be seen that the sp. gr. is considerably lower, indicating a differing structure. The color reaction also shows that we have to do with a peculiar structure.

The work of Deussen and Philipp,¹ Semmler and Spornitz,² Semmler and Jakubowicz,³ on the sesquiterpenes of gurjun oil, gives interesting data for comparison with the dihydro-sesquiterpene from azulene. Deussen and Philipp found that oil of gurjun consists of two sesquiterpenes. Semmler and Jakubowicz then showed that these were both tricyclic, the crude oil, on reduction by hydrogen and platinum, absorbing only two hydrogen atoms and yielding a dihydro product with sp. gr. at 20° 0.909; n_D 1.49; b. p. 115–117 at 7 mm. They succeeded further in separating the crude oil with the following characters: sp. gr. 0.922; O. R. —55°; n_D 1.507, into the two tricyclic sesquiterpenes:

β -Gurjunene; sp. gr., 0.9348; O. R. + 74.5°; n_D 1.50275. α -Gurjunene, sp. gr., 0.918; O. R. —95°.

The β -gurjunene, which forms about 33% of the oil, resembles cedrene closely, but is not chemically identical. It does not give the color reactions characteristic of crude gurjun oil, and yields no blue oil on heating under pressure. Its reduction product by hydrogen and platinum has the characters:

Sp. gr., 0.9258; n_D 1.49775; b. p., 120° at 8 mm.

¹ *Ann.*, 374, 105 (1910).

² *Ber.*, 47, 1029 (1914).

³ *Ibid.*, 47, 1141 (1914).

α -Gurjunene gives the color reactions of the crude oil, and on heating under pressure with air or oxygen yields a blue oil.

From these data the approximate constants of the dihydro- α -gurjunene can be derived: Sp. gr. at 20° 0.900; n_D 1.492, which agree with those of the dihydro derivative from azulene. Summing up the characteristics of α -gurjunene, we find: (1) it gives the color reactions characteristic of crude gurjun oil; (2) it yields azulene on heating under pressure with oxygen; (3) it is reduced to a tricyclic dihydro-sesquiterpene with constants and chemical behavior such as color reactions, similar to those of the reduction product from azulene. All these properties differ from those of other tricyclic sesquiterpenes such as β -gurjunene and cedrene. It is possible that other sesquiterpene types may be inverted by the reagents used, and so show some of the same properties.

It seems quite probable, however, that the α -gurjunene is the type which produces azulene, and that the dihydro-sesquiterpene formed by the complete reduction of azulene is identical with dihydro- α -gurjunene, although further experiments are necessary to demonstrate any such identity.

In the present state of our knowledge of the structure of the sesquiterpenes and the experimental data on azulene, an attempt to ascribe a structural formula to the latter is necessarily purely speculative. Certain bases for a discussion of the possibilities are, however, not lacking, for instance:

(1) It is closely related to the sesquiterpenes in structure, as shown by the mode of formation and its reduction product.

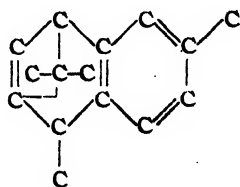
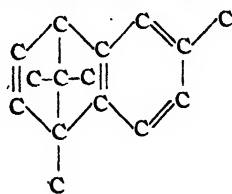
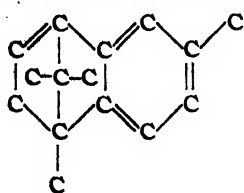
(2) It is tricyclic and consequently contains four ethylene bonds.

(3) It possesses an aromatic nucleus, indicated by the ready formation of a picrate.

(4) It contains no hydroaromatic conjugate double bonds, since it is not reducible by sodium in alcohol.

(5) It has a peculiar arrangement of the double bonds which accounts for its intense color, such color intensity being exhibited by no hitherto discovered hydrocarbon.

If we take, for the time being, the type formulae suggested by Semmler, and consider the possibilities of oxidizing to a tricyclic, tetra- or pentocyclic molecule $C_{15}H_{18}$, which could be reconciled with the above requirements, we arrive at structures such as the following:



Whether or not the azulene molecule has some such structure, can only be determined by further study, perhaps from its oxidation products. Its formation from the sesquiterpenes can aid but little in this direction, so long as their structure is so little known, but a synthesis from substances of known structure does not seem impossible. In this connection the formation of the blue oil by the dry distillation of calcium adipate, (Hentschel and Wislicenus),¹ is interesting. Such a synthesis would seem to give the greatest promise in indicating the structure of this remarkable substance, and would at the same time give additional evidence as to the structure of the sesquiterpenes to which it is related.

Two obvious typographical errors crept into the first article on azulene, in connection with the molecular weight determination (p. 169). This determination was made by Dr. Farnau of New York University, and the values found agreed well with those calculated for $C_{15}H_{18}$, 198.

BAYONNE, N. J.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF THE SO-CALLED DITHIOURIMIDO-ACETYLACETONE.

BY WILLIAM J. HALE.

Received April 8, 1915.

The principal product resulting from the condensation of urea and acetylacetone has been called by Evans² acetylacetone-urea. The constitution of this substance, a 2-ketopyrimidine, has been thoroughly investigated by de Haan and others.³ At the same time de Haan recognized in the reaction product the presence of two new distinct substances. One of these new compounds was found to be a 2-ketopyrimidine-urea and identical in all respects with the second product which Evans had obtained by the use of a slightly acid condensing medium, and to which he had assigned the structure corresponding to a diurimido-acetylacetone. In all cases it is to be assumed that, during these condensations, one molecule of acetylacetone and one molecule of urea proceed directly to the formation of a pyrimidine ring, and that afterwards another molecule of urea condenses with this pyrimidine ring to form either a simple ureide derivative or a second ring leading to a compound of the diureino type.

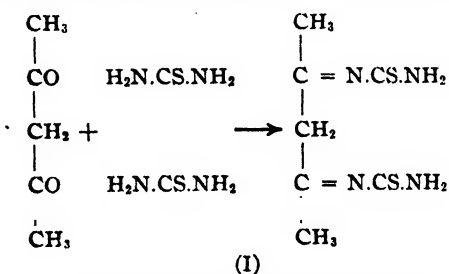
According to Evans, the principal product in the condensation of thio-urea and acetylacetone is a 2-thiopyrimidine [II] (acetylacetone-thio-urea). By use of a small amount of acid he further secured the product corresponding to his diurimido-acetylacetone, namely, dithiourimido-

¹ *Ann.*, 275, 312 (1893).

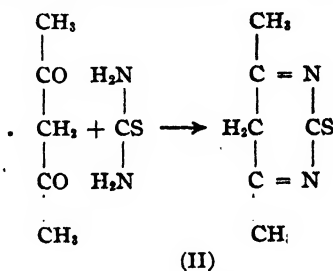
² *J. prakt. Chem.*, [2] 48, 489 (1893).

³ *Rec. trav. chim.*, 27, 162 (1908); *THIS JOURNAL*, 36, 104 (1914).

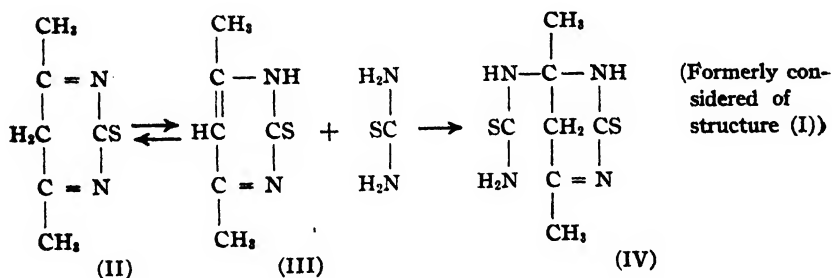
acetylacetone (I). This 2-thiopyrimidine has lately¹ been shown to be possible of existence in a tautomeric form (III) but to a much less extent than that of the 2-ketopyrimidine. The dithiourimido product, however, received but little attention by Evans and has been known only in the form of a salt. It seemed more than likely that the products obtained from urea and acetylacetone might find their counterparts in the condensation mixtures from thiourea and this same ketone; consequently, a study of this condensation was undertaken to establish the exact constitution of Evans' dithiourimido-acetylacetone and at the same time to search for a third product of the diureino type (VI). The outlines of these condensations are given first as described by Evans in (I) and (II), and later as here to be interpreted in the light of previous work, especially that of de Haan² upon acetylacetone and the analogous substance urea.



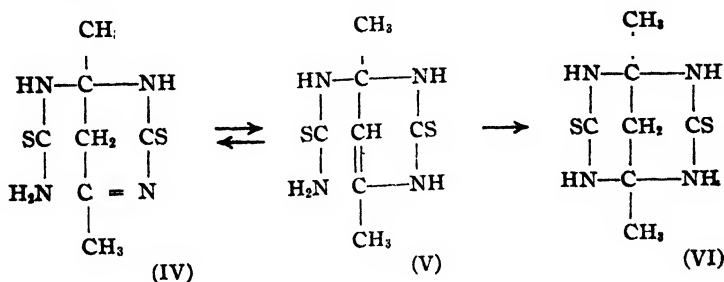
Dithiourimido-acetylacetone (Evans).



Acetylacetone-thiourea (Evans).



(Formerly considered of structure (I))



¹ THIS JOURNAL, 37, 594 (1915).

² *Loc. cit.*

The distinctive property of acetylacetone-thiourea in failing to release its sulfur atom, even by prolonged action of such desulfurizing agents as mercuric oxide and basic lead acetate, distinguishes this type of sulfur directly bound to the ring as markedly different from that form usually present in a side chain and so readily split off by these same agents; on the other hand, this property stamps it as closely similar to sulfur held within the ring itself. This inactivity of the sulfur atom is due to the presence of the strongly negative nitrogen atoms at either side of the carbon which holds it. When one of these nitrogen atoms carries an alkyl substituent¹ this property is lost and the sulfur can be completely removed. The action of chloroacetic acid,² however, is sufficient to remove this sulfur even in the firmly bound condition previously described. Prolonged boiling of an aqueous solution of acetylacetone-thiourea and chloroacetic acid yielded acetylacetone urea.³

The product prepared by Evans and called dithiourimido-acetylacetone (I) was obtained, as a hydrochloride, when just a few drops of conc. hydrochloric acid were added to an absolute alcoholic solution of the reacting components. The free base is most readily prepared by gently warming a concentrated aqueous solution of thiourea (2 mol) and acetylacetone (1 mol) at the temperature of the steam bath. This product is of a light yellow color and when converted into a hydrochloride by the action of hydrochloric acid affords a salt which corresponds exactly to the hydrochloride obtained by Evans, melting at 219°. The method employed by Evans leads to the formation of both this product just mentioned and the hydrochloride of acetylacetone-thiourea, hence it is not to be recommended. The free base prepared directly and in comparatively pure state is always yellow, but when allowed to form by a slow condensation, without the aid of heat and in the dark, possesses a much lighter yellow color. There is, however, no other point of difference between the products.

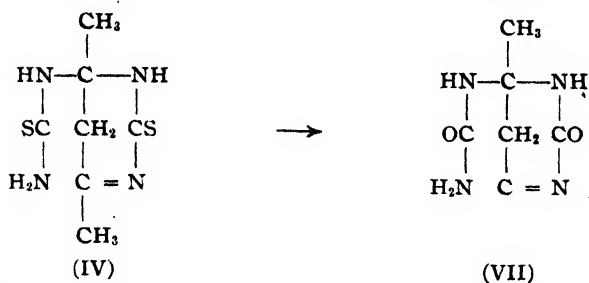
This so-called dithiourimido-acetylacetone readily gave up a part of its sulfur to mercuric oxide. In order to remove all of the sulfur the prolonged action of chloroacetic acid in aqueous solution was employed. From the reaction product was obtained a good yield of 2-ketopyrimidine-urea (VII) melting at 197° and in every respect identical with the product formerly known as diurimido-acetylacetone. Desulfurization must have proceeded as here shown.

The structure, therefore, is clearly indicated by this transformation into the well-known 2-ketopyrimidine-urea. In order to check this point there remained only to condense one molecule of thiourea with acetyl-

¹ Hale and Williams, *THIS JOURNAL*, 37, 599 (1915).

² Wheeler and Liddle, *Am. Chem. J.*, 40, 549 (1908).

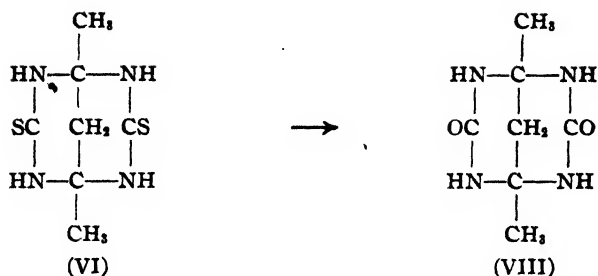
³ Hale and Williams, *THIS JOURNAL*, 37, 598 (1915).



acetone-thiourea and obtain the original product. This condensation proceeded well when these two substances were brought together in concentrated aqueous solution without the presence of condensing agent. The light yellow precipitate formed was identical in all respects with the so-called dithiourimido-acetylacetone, or 2-thiopyrimidine-thiourea, melting at 192° . There can be, therefore, no doubt as to the structure of the compound—that of a monothioureide of the base acetylacetone-thiourea. In the presence of strong acids in alcoholic solution, Evans obtained the more or less insoluble salts of acetylacetone-thiourea. When, however, acids are absent the aqueous, as well as alcoholic, solution of these reacting components favors the formation of the less soluble thiopyrimidine-thioureide. In the absence of alcohol, water and other condensing media, thiourea and acetylacetone yield both the thiopyrimidine and the thiopyrimidine-thioureide, but chiefly the latter, owing to its greater insolubility in acetylacetone itself.

Since the structure of dithiourimido-acetylacetone found its counterpart in the structure of 2-ketopyrimidine-urea, there seemed a possibility that a third product might be expected to accord with a 2,4-dithioureino-pentane, Formula VI. The analogous keto derivative was found to be present in very small quantities in the reaction product obtained by heating urea and acetylacetone upon a water bath. It remained always as the portion insoluble in alcohol. de Haan obtained small portions of this substance, decomposing at 290° , when urea and acetylacetone were allowed to condense in aqueous solution. Thiourea and acetylacetone were heated together under many conditions of temperature and pressure and scarcely a trace of a portion insoluble in alcohol could be procured. Several months' standing of absolute alcoholic solutions of thiourea and acetylacetone did yield a product practically insoluble in alcohol. This substance decomposed at 265° and refused to release its sulfur to mercuric oxide or basic lead acetate. Prolonged action of chloroacetic acid removed all of the sulfur and converted it into the 2,4-diureinopentane (VIII) of de Haan, decomposing at 290° .

The third possibility, therefore, in the condensation of thiourea and acetylacetone is fulfilled and a two-ring compound produced. The



great difficulty in producing any appreciable amount of this dithioureine would seem to rest upon the increased difficulty for the 2-thiopyrimidine-thiourea (IV) to undergo further transformation to yield another imino nitrogen (V), a necessary step preliminary to the second ring formation (V) to (VI). As previously reported¹ the stable form of 2-thiopyrimidine itself is undoubtedly quinoid in structure, and this transformation of the ring to produce a second imino form would be attended with greater and greater difficulty.

Experimental Part.

When concentrated sulfuric acid is added to an alcoholic solution of acetylacetone and thiourea, crystals of acetylacetone-thiourea hydro-sulfate soon make their appearance. The constitution and properties of the free base, liberated by the action of barium carbonate upon this salt, have previously been described.¹ On the other hand, when only a very small quantity of acid is used as the condensing agent in this reaction there results, according to Evans, a salt of dithiourimido-acetylacetone. This latter will now be described as a thiopyrimidine-thioureide.

6-Thioureido-4,6-dimethyl-2-thio-1,2,5,6-tetrahydropyrimidine (IV).—The condensation of thiourea and acetylacetone, upon the addition of a few drops of concentrated hydrochloric acid to the absolute alcoholic solution, resulted in the slow formation of a hydrochloride melting at 219°. Three days were required for the completion of the reaction as described by Evans. Under these conditions, however, a variable amount of acetylacetone-thiourea hydrochloride is always formed and naturally constitutes a part of the crystalline product. Many crystallizations are necessary to remove the last traces of this latter salt. As the free base from the former salt was not isolated by Evans, it seemed advisable to attempt its preparation by a condensation in the absence of acids. Accordingly thiourea and acetylacetone were brought together in an alcoholic as well as in an aqueous solution and in each case, after a few days, small, yellow crystals of the free base appeared. The slight solubility of thiourea in absolute alcohol materially lessened the quantity of condensation product formed, but with water as the medium a relatively large yield was obtained. Dur-

¹ *Loc. cit.*

ing this condensation in aqueous solution a considerable portion of colorless crystals of thiourea separate, but with the gradual increase in amount of thiourea precipitated a further solution of thiourea and subsequent condensation proceeds. After several weeks' standing in the dark an excellent yield of light lemon-yellow monoclinic prisms was removed. Gently warming the reaction mixture to effect complete solution from time to time, secures a more rapid conversion of thiourea into the final product; consequently, the following procedure was adopted as giving the best results.

Three grams (2 mol) of thiourea were dissolved by warming in 5 cc. of water and 2.5 g. (excess of 1 mol) of acetylacetone added. The test tube containing the mixture was then sealed and placed in a steam bath (98°) from 10 to 12 hours. Upon cooling the reaction mixture, 3.3 g. of yellow condensation product separated and from the mother liquor an additional 0.6 g. was collected, bringing the percentage of yield to 91% of the theoretical. The color of this product was of a more decided yellow than that possessed by the free base resulting through a slow condensation in the dark. Repeated crystallizations under varying conditions failed to reduce materially this yellow color of the product, whereas with the light lemon-yellow colored product, repeated crystallizations rendered it almost, but never quite, colorless. These two products are, however, identical in crystalline form and in all other respects. The melting point of this thiopyrimidine-thiourea is 192°. 4,6-Dimethyl-2-thiopyrimidine-thiourea is fairly soluble in water or alcohol, crystallizing from either, but better from the latter, in monoclinic prisms. It is only slightly soluble in acetone and practically insoluble in chloroform, ethyl acetate, benzene, ether or ligroin.

An aqueous solution of this substance readily blackens mercuric oxide or basic lead acetate—a point distinguishing it at once from acetylacetone-thiourea, and indicating the presence of a free thiourea group.¹

The formation of this thiopyrimidine-thiourea presupposes the intermediate formation of a thiopyrimidine in the reaction mixture and the subsequent condensation of this product and a second molecule of thiourea. The thiopyrimidine that must be formed, *i. e.*, acetylacetone-thiourea, is very soluble in chloroform and hence may readily be removed from mixtures of these substances when present. Under the conditions of the reactions here given the final crystalline products, by extraction with chloroform, failed to show the presence of any acetylacetone-thiourea. The presence therefore of water alone (and alcohol as well) as condensing medium, may be looked upon as facilitating the production of this thiopyrimidine-thiourea at the expense of the thiopyrimidine in process of formation.

¹ *Loc. cit.*

When a solution of 1 part of thiourea in 10 parts of acetylacetone alone is heated to boiling under a reflux condenser for 5 or 6 hours and then allowed to stand several days, these same yellow crystals of the thiopyrimidine-thioureide make their appearance. With less decomposition the same end is accomplished by warming the two ingredients in a sealed test-tube for 24 hours at about 98° (steam bath). The yellow prisms begin to separate during the heating, and upon cooling they are precipitated in an excellent state of purity. Washing with cold water removed no trace of thiourea. One gram of thiourea and 10 g. of acetylacetone yielded thus 1 g. of the thioureide crystals. When the red mother-liquor was evaporated to dryness upon a steam bath and the residue digested with chloroform, about 0.6 g. of the intermediate acetylacetone-thiourea was dissolved out. The portion insoluble in the chloroform (0.2 g.) consisted of the thioureide alone and increased its production in this case to 1.2 g. We may conclude, therefore, that the absence of water in the condensing medium makes possible the formation of both products: acetylacetone-thiourea and thiopyrimidine-thioureide, and that the favored formation of the latter, even in the presence of so large an excess of acetylacetone, is undoubtedly due to its slight solubility in this medium.

Preparation of 2-Thiopyrimidinethiourea from Acetylacetone-thiourea.

—When conc. aqueous solution of thiourea (1 mol) and acetylacetone (1 mol) are brought together at room temperature, prisms of thiopyrimidine-thiourea soon separate. These crystals when purified melt at 192° and are identical with the product obtained by condensing 2 molecules of thiourea and 1 molecule of acetylacetone in aqueous solution. The possibility of a molecular type of compound between these two component parts was at once dismissed. Many crystallizations from various solvents as well as many extractions with chloroform (in order to withdraw the readily soluble acetylacetone-thiourea portion) proved futile. The product is without water of crystallization.

0.1346 g. subst. gave 0.1912 g. CO_2 and 0.0686 g. H_2O .

Calc. for $\text{C}_7\text{H}_{12}\text{N}_4\text{S}_2$: C, 38.85%; H, 5.59%. Found: C, 38.75%; H, 5.70%.

In order to identify the hydrochloride obtained by Evans according to his mode of condensation, a portion of thiopyrimidine-thiourea was dissolved in water and treated with a little concentrated hydrochloric acid. The hydrochloride thus prepared crystallized from alcohol in irregular yellow prisms melting at 219° , checking exactly the observations reported by Evans. An analysis also accorded with the same result. There can be no doubt, therefore, as to the identity of the two products as hydrochlorides and hence, also, as free bases.

0.2220 g. HCl salt gave 0.1252 g. AgCl.

Calc. for $\text{C}_7\text{H}_{12}\text{N}_4\text{S}_2\cdot\text{HCl}$: HCl, 14.42%. Found: HCl, 14.35% (Evans, 14.06%).

Replacement of Sulfur by Oxygen.—When 1 g. of thiopyrimidine-thiourea is boiled with 1.5 g. of chloroacetic acid in 15 cc. of water for five hours under reflux condenser, the sulfur atom of the thiourea side chain, as well as that directly united to the pyrimidine nucleus, is replaced by oxygen. The reaction mixture, evaporated to dryness, was extracted with absolute alcohol and the residue almost neutralized with potassium hydroxide solution, when it was again evaporated to dryness over the steam bath and the final residue extracted with benzene. Colorless crystals melting at 197° were obtained upon removal of the benzene. This substance proved to be identical with the 2-ketopyrimidine-urea (VII) of de Haan. Mixtures of the two showed this constant melting point and their solubilities also exactly accorded. de Haan¹ proved that urea and acetylacetone-urea condensed in alcoholic solution to produce this product melting at 197° and thus further proof of the constitution of the analogous thiopyrimidine-thiourea is established.

2,4-Dithioureinopentane (VI).—In repeating the work of earlier investigators de Haan showed that when urea and acetylacetone were heated together a very small quantity of a substance insoluble in alcohol could be obtained. The formula he assigned to this product is that of a 2,4-diureinopentane (VIII) and resulted upon the further intramolecular condensation of 2-ketopyrimidine-urea. In working upon thiourea and acetylacetone alone, no appreciable amount of a similar substance could be prepared.^b This type of compound, however, was isolated in three or four instances where thiourea and acetylacetone in absolute alcoholic solution had been allowed to stand in stoppered tubes over the summer months, more or less exposed to the sunlight. The dark yellow crystalline mass was powdered and extracted with boiling absolute alcohol. The alcohol removed the thiopyrimidine-thiourea, but left undissolved a colorless crystalline product insoluble in practically all reagents. It is only slightly soluble in acetone or water, but of course soluble in acids. It may be crystallized from acetylacetone in which it is fairly soluble. The decomposition point is about 265° .

0.1142 g. subst. gave 27.3 cc. N_2 (25.5° and 746.6 mm. over H_2O).
Calc. for $C_7H_{12}N_6S_2$: N_2 , 25.91%. Found: 26.08%.

As this substance does not blacken mercuric oxide, we may consider that its two sulfur atoms are in two separate positions similar to that one already indicated for 2-thiopyrimidine. By the action of chloroacetic acid, however, the compound is freed of all sulfur. The aqueous chloroacetic acid solution, after five hours' boiling with this product, was evaporated to dryness, extracted with absolute alcohol and the residue treated with moist silver oxide and again evaporated. Extraction of the final

¹ *Rec. trav. chim.*, 27, 175 (1908).

product with water gave a colorless substance, identical with that compound decomposing at 290° and obtained by de Haan as stated above.

It is exceedingly difficult to procure any appreciable quantity of this dithioureinopentane. The greater ease by which the diureinopentane may be procured is, in one respect at least due to the practical insolubility of this latter product in acetylacetone.

For the kind assistance of Mr. Frank C. Vibrans upon the analytical data in this paper the author desires to express his indebtedness.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF COLUMBIA UNIVERSITY AND THE HARRIMAN RESEARCH LABORATORY. No. 249.]

INOSITE AND PINITE AND SOME OF THEIR DERIVATIVES.

By EDWARD G. GRIFFIN AND J. M. NELSON.

Received April 12, 1915.

Inosite and its derivatives possess considerable interest. The sugar itself is interesting, due to its wide occurrence in nature and possible important physiological functions, and also due to its close relationship in chemical constitution to the hexoses and some hydroaromatic compounds. The synthesis of the derivatives of inosite, when compared to the synthesis of the analogous derivatives of a substance like glucose, affords a comparison of the effect on the properties of a hexose in which the carbons are arranged in the form of a closed ring instead of an open chain. The derivatives might also prove valuable in the study and synthesis of many complex substances like phytin and some of the tannins, which yield, on decomposition, inosite or closely related products like phloroglucin and quinic acid, $C_6H_7(OH)_4COOH$.

Derivatives of inosite mentioned in literature prior to this investigation are: the hexacetate, hexabenzoate,¹ hexa- and trinitrates,² monobromopentacetate, two isomeric dibromotetraacetates, and mono- and dibromohydrins.³ While this work was in progress, Müller published a second article describing a triacetate, three isomeric chlorohydrin-pentacetates, a chlorohydrintriacetate, a chlorohydrin, two new isomeric inosites, which he called iso and ψ ; and an iso-inosite hexacetate and tetrabenzoate.⁴

By the action of acetyl bromide on inosite the following products were obtained: Bromopentacetylcyclohexanpentol, $C_6H_5Br(OCOCH_3)_5$;⁵ two

¹ Maquenne, *Compt. rend.*, 104, 297 (1887).

² Vohl, *Ann.*, 101, 55 (1857).

³ Müller, *J. Chem. Soc.*, 91, 1780 (1907).

⁴ *J. Chem. Soc.*, 101, 2383 (1912).

⁵ The names ascribed to the esters and derivatives of inosite mentioned in literature are sometimes not satisfactory, and for that reason the Geneva system of nomenclature has been adopted.

isomeric dibromotetracetylcyclohexantetrols, $C_6H_6Br_2(OCOCH_3)_4$, called α and β for distinction in name; dibromocyclohexantetrol, $C_6H_6Br_2(OH)_4$; dibromodiacetylcyclohexantetrol, $C_6H_6Br_2(OH)_2(OCOCH_3)_2$; dibromotriacetylcyclohexantetrol, $C_6H_6Br_2(OH)(OCOCH_3)_3$; and tribromotriacetylcyclohexantetrol, $C_6H_6Br_3(OCOCH_3)_3$. The first four products mentioned were identical with those obtained by Müller by glacial acetic acid, hydrogen bromide and hexacetylcyclohexanhexol, although the melting points of three of them were different.

Acetyl chloride gave products, none of which appeared to be identical with those obtained by Müller. They are: chloropentacetylcyclohexanpentol, $C_6H_6Cl(OCOCH_3)_5$; α - and β -dichlorotetracetylcyclohexantetrol, $C_6H_6Cl_2(OCOCH_3)_4$; and dichlorocyclohexantetrol, $C_6H_6Cl_2(OH)_4$. Another substance, probably dichlorodiacetylcyclohexantetrol, $C_6H_6Cl_2(OH)_2(OCOCH_3)_2$, was also obtained.

Many additional organic acyl derivatives were also prepared. Besides hexacetylcyclohexanhexol and hexabenzoylcyclohexanhexol, two isomeric hexacetylcyclohexanhexols which have been distinguished in name by the prefixes, α and β ; pentabenzoylcyclohexanhexol, $C_6H_6(OH)(OCOC_6H_5)_5$; tetrabenzoylcyclohexanhexol, $C_6H_6(OH)_2(OCOC_6H_5)_4$; hexanisylcyclohexanhexol, $C_6H_6(OCOC_6H_4OCH_3)_5$; pentanisylcyclohexanhexol, $C_6H_6(OH)(OCOC_6H_4OCH_3)_5$; hexacinnamoylcyclohexanhexol, $C_6H_6(OCOC_2H_2C_6H_5)_5$; two isomeric pentacinnamoylcyclohexanhexols, α and β , $C_6H_6(OH)(OCOC_2H_2C_6H_5)_5$; hexa-*m*-nitrobenzoylcyclohexanhexol, $C_6H_6(OCOC_6H_4NO_2)_5$; and penta-*m*-nitrobenzoylcyclohexanhexol, $C_6H_6(OH)(OCOC_6H_4NO_2)_5$, were obtained.

Up to the time of this investigation, no alkyl derivatives of inosite had been synthesized. By alkylation of inosite and subsequent purification by means of the intermediate alkyl acetyl derivatives, the following were obtained: monomethylcyclohexanhexol, $C_6H_6OCH_3(OH)_5$; a syrup, probably dimethylcyclohexanhexol, $C_6H_6(OCH_3)_2(OH)_4$; diethylcyclohexanhexol, $C_6H_6(OC_2H_5)_2(OH)_4$; and a syrup, probably monoethylcyclohexanhexol, $C_6H_6OC_2H_5(OH)_5$. Others were obtained as syrups, but so far not sufficiently pure to definitely decide on their true composition. The alkyl acetyl derivatives obtained were, pentacetylmethylcyclohexanhexol, $C_6H_6OCH_3(OCOCH_3)_5$; tetracetyldimethylcyclohexanhexol, $C_6H_6(OCH_3)_2(OCOCH_3)_4$; pentacetylethylcyclohexanhexol, $C_6H_6OC_2H_5(OCOCH_3)_5$; tetracetyldiethylcyclohexanhexol, $C_6H_6(OC_2H_5)_2(OCOCH_3)_4$; and triacetyldimethylcyclohexanhexol, $C_6H_6(OCH_3)_2(OH)(OCOCH_3)_3$.

From pinite itself the following acyl derivatives were also prepared: pentacetylmethylcyclohexanhexol, $C_6H_6OCH_3(OCOCH_3)_5$; pentabenzoylmethylcyclohexanhexol, $C_6H_6OCH_3(OCOC_6H_5)_5$; pentanisylmethylcyclo-

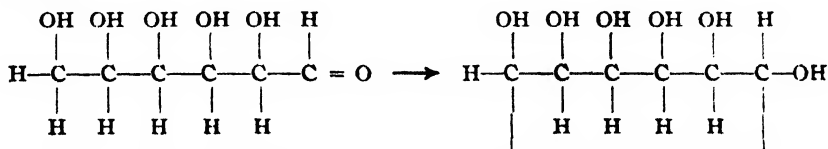
hexanhexol, $C_6H_5OCH_2(OCOC_6H_5OCH_2)_5$; and pentacinnamoylmethylcyclohexanhexol, $C_6H_5OCH_2(OCOC_2H_2C_6H_5)_5$.

Nitration and alkylation yielded syrups, which could not be crystallized and so far have not been identified.

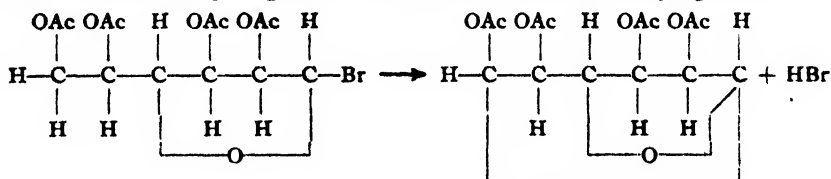
In treating pinite with acetyl bromide, as was done in the case of inosite, no halide esters of pinite were obtained but, instead, halide esters of inosite. This shows that the methoxy groups were attacked by the acetyl bromide as well. The following inosite esters were obtained: α - and β -dibromotetracetylcyclohexantetrol and dibromocyclohexantetrol.

The object in the beginning of this investigation was the synthesis of inosite or compounds closely related to it. However, all the attempts proved unsuccessful, and their descriptions are only indicated briefly as follows:

1. Aldolization between the carbonyl and primary alcohol groups in glucose.



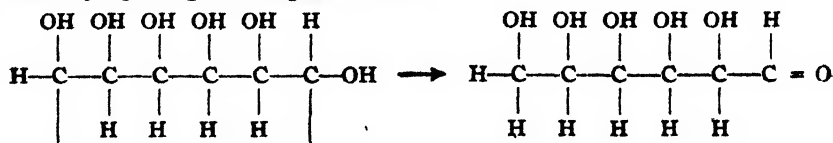
2. Removal of hydrogen bromide from bromotetracetyl glucose.



Attempts were also made to repeat the work of Rosenstiehl,¹ in which he claimed to have obtained sugars by treating benzene hexachloride with silver acetate, but no reaction was found to take place.

Neither was it possible to repeat the work of Carius,² who prepared a cyclic sugar, phenose, $C_6H_{12}O_6$, by the hydrolysis of benzene trichlorohydrin, $C_6H_6(\text{Cl OH})_3$.

Having failed to obtain any information as to the stereo-configuration of inosite by tying up the end carbon atoms of an open chain hexose molecule, the opposite was undertaken. It was hoped to pass from inosite to a hexose by opening the ring as follows:



¹ *Compt. rend.*, **54**, 178 (1862).

² *Ann.*, **136**, 323 (1866).

and thus the stereo-configuration might be established by noticing the particular hexose formed.

As yet, the identity of the products obtained has not been ascertained and will be further investigated.

Experimental Part.

Although the synthesis of inosite in this laboratory has thus far been unsuccessful, "steep water,"¹ a by-product obtained in the manufacture of corn products, has been found to offer a source for inosite in sufficient quantities for the study and preparation of several of its derivatives.

Procedure: In a vat containing 42 liters of "steep water," (sp. gr. 1.246) were poured 125 liters of boiling water containing 20 kg. of barium hydroxide. The precipitate was separated by means of a filter press and washed till the filtrate was colorless. The press cake obtained was transferred to a vat and stirred with 40 liters of water containing 12 kg. of commercial sulfuric acid. The dark red mixture was pumped through a filter press and washed with water till the filtrate totaled 100 liters. The solution was then evaporated to 12 liters, giving a heavy reddish black liquid (sp. gr. 1.484, b. p. 125°), containing approximately 33% sulfuric acid. This liquid was divided into eight portions of 1500 cc. each. A portion was placed in a tall meal jar and heated in a steam digester under a pressure of 5 atmos. at 150° for 4 hours. The resulting black liquid was diluted with water, filtered from the carbonaceous material and thoroughly washed. The red solution was diluted to 9 liters, three equal portions of which were placed in large jars. To each were added 5 liters of a hot aqueous solution, containing 1300 g. of barium hydroxide, and the resulting curdy, grayish precipitate vigorously stirred. The precipitate was filtered through large fluted filter papers with parchmented tips, and washed by boiling with water. The combined pale yellow filtrates were evaporated to 400 cc., yielding a dark, reddish green fluorescent liquid. While still hot, 1200 cc. of glacial acetic acid were added, which caused the inosite to separate on cooling. To complete the crystallization, the mixture was placed in the ice box over night. It was filtered by suction and washed with glacial acetic acid, which dissolved out the coloring matter, and finally with alcohol. A beautiful, white, crystalline product of practically pure inosite remained. Yield, 46 g.

The use of glacial acetic acid in precipitating the above solution was found to be very advantageous, since it removes the gums and coloring matter, which alcohol does not do. For the further purification of inosite, the following method was found to work satisfactorily: Fifty grams of crude inosite were dissolved in 200 cc. of water, a few drops of sulfuric

¹ The steep water was kindly furnished by the Corn Products Refining Company. Its use as a source for the preparation of inosite was suggested by Dr. A. R. Rose, recently of the New York Agricultural Experiment Station.

acid added to remove any barium, the solution was concentrated to 75 cc. and alcohol added to turbidity. When cold, 200 cc. of alcohol and 50 cc. of ether were added and the mixture placed in the ice box over night. The inosite separated nearly quantitatively in little, feathery crystals, melting at 225°.

Each of remaining seven portions were treated in the same manner. Some additional inosite was obtained from the acetic acid and alcoholic mother liquors, giving a total yield of 368 g.

Inosite, containing two molecules of water, crystallizes from water or dilute acetic acid in colorless rhombic prisms, melting at 225°, and charring slightly above this temperature. It is optically inactive and unfermentable.

Action of Acetyl Bromide on Inosite.

The fact that glucose and acetyl bromide yield bromotetracetyl glucose suggested that halide esters of inosite might be obtained in a similar manner. Accordingly, inosite was treated with acetyl bromide but only hexacetylcyclohexanhexol was obtained. It proved, however, to be an excellent method for the preparation of hexacetylcyclohexanhexol, giving better yields in a shorter time than by any of the methods heretofore used.

Acetylation of Inosite by means of Acetyl Bromide.—Three grams of dry inosite and 18 g. of acetyl bromide were gently heated together in a flask connected with a ground-in glass condenser. In ten minutes, a clear, red solution resulted which was slowly poured into water, whereupon a semicrystalline mass separated. The mass was filtered off and recrystallized from hot alcohol as a scaly crystalline product. Yield, 7 g. No lower acetylated derivatives were obtained from the mother liquors.

Since inosite is not easily decomposed by concentrated acids under pressure, the reaction was also carried out in a sealed tube. Under these conditions, however, no hexacetylcyclohexanhexol was obtained, but, instead, several bromo esters of inosite.

In a large glass tube, immersed in a freezing mixture in order to retard the reaction until the tube was sealed, 25 g. of inosite (dried at 110°) and 100 g. of acetyl bromide were placed. The sealed tube was heated for 6 hours at 120°. Care was taken in opening the tube to prevent loss of the contents due to frothing. The dark red syrup together with the glass tube, which was broken in pieces to regain the adhering syrup, was transferred to a flask and the mass evaporated in a vacuum on a water bath. The residue was taken up with a little absolute alcohol and again evaporated and finally crystallized from a large amount of alcohol. The crystals were dried on a porous plate and gave a yield of 18 g. and were designated (A). On evaporating the filtrate to half its volume by means of a current of air, a precipitate of smaller crystals gradually separated. These were filtered off and amounted to 12 g. (B). The dark red filtrate was further concentrated by a current of air to the point at which an oil began to form. Five grams of a crystalline precipitate (C) were obtained. The filtrate now measured about 75 cc. and on standing over night separated into two layers. The upper, a light red solution having a strong odor of ethyl acetate yielded 2 g. of a fine crystalline product (D). The lower layer was a black oil. This was combined with the filtrate from (D), alcohol and animal charcoal were added, and the mixture boiled for 6 hours. A pale yellow solution (E) was obtained, which did not crystallize. It was placed in the ice box over calcium chloride for a few days.

The various portions were mixtures and were best separated by fractional crystallization from alcohol. As there was no well-defined line of separation, the crystallization was carefully watched, and each kind of crystals filtered off as they formed. Two recrystallizations usually resulted in a constant melting point being obtained.

(A) consisted of bromopentacetylcyclohexanpentol and α -dibromotetracetylcyclohexantetrol. (B) was a mixture of α - and β -dibromotetracetylcyclohexantetrols and a small amount of dibromotriacetylcyclohexantetrol. From (C) was obtained dibromotetracetylcyclohexantetrol and dibromodiacetylcyclohexantetrol. (D) consisted of only dibromodiacetylcyclohexantetrol. (E) yielded a small amount of tribromotriacetylcyclohexantriol, as a fine, white powder. The mother liquors from (E) after standing in the ice box for several weeks changed to an opaque mass. It was freed from adhering syrup by crushing on a porous plate. This crude product, which amounted to 15 g., was boiled with benzene, which dissolved the coloring material and any tribromotriacetylcyclohexantriol, and was finally obtained as a white powder which proved to be dibromocyclohexantetrol.

Bromopentacetylcyclohexanpentol, crystallizes from boiling alcohol in fine, indistinct crystals, melting sharply at 240° . It is soluble in chloroform, ether, acetone and benzene, and is insoluble in water, ligroin or methyl alcohol. It is optically inactive.

Calc. for $C_6H_8Br(OCOCH_3)_5$: Br, 17.66%; C, 42.38%; H, 4.64%. Found: Br, 17.72%; C, 42.23%; H, 4.69%.

α -Dibromotetracetylcyclohexantetrol, differs from its isomer in its crystalline form and is less soluble. It separates as scaly crystals from alcohol and as long, flat, colorless prisms from benzene. It melts at 225° to a colorless liquid. It is optically inactive.

Calc. for $C_6H_8Br_2(OCOCH_3)_4$: Br, 33.75%; C, 35.44%; H, 3.78%. Found: Br, 33.83; C, 35.35; H, 3.83.

β -Dibromotetracetylcyclohexantetrol, crystallizes best from alcohol, forming large, brilliant, rhombic prisms, melting at 130° to a clear, colorless liquid which forms a crystalline foliated solid on cooling. It is soluble in benzene, chloroform, ether, glacial acetic acid, and ethyl acetate, and insoluble in water. It is optically inactive.

Calc. for $C_6H_8Br_2(OCOCH_3)_4$: Br, 33.75%; C, 35.44%; H, 3.78%. Found: Br, 33.71; C, 35.29; H, 3.72.

Dibromotriacetylcyclohexantetrol, crystallizes from alcohol in small, slender prisms, m. p. 124° . On acetylation, it yields β -dibromotetracetylcyclohexantetrol.

Calc. for $C_6H_8Br_2(OH)(OCOCH_3)_3$: Br, 37.04%. Found: 37.20.

Dibromodiacetylcyclohexantetrol, crystallizes from alcohol in clusters of soft, white needles, melting at 214° with decomposition. It is soluble

in alcohol, acetone and ethyl acetate, less soluble in ether or glacial acetic acid and insoluble in water, chloroform, and benzene. It is optically inactive.

Calc. for $C_6H_6Br_2(OH)_2(OCOCH_3)_2$: Br, 41.02%; C, 30.77%; H, 3.59%; Acetyl, 30.26%. Found: Br, 40.78 and 40.83; C, 30.59 and 30.88; H, 3.42 and 3.65; Ac,¹ 30.28 and 30.33.

On acetylation, dibromodiacetylcyclohexantetrol yields β -dibromotetracetylcyclohexantetrol.

Tribromotriacetylcyclohexantriol, crystallizes from benzene in microscopic plates, melting at 180° . It is soluble in alcohol, chloroform, benzene, acetone and glacial acetic acid and insoluble in water and in ligroin. It is optically inactive.

Calc. for $C_6H_6Br_3(OCOCH_3)_3$: Br, 48.48%; C, 29.09%; H, 3.33%. Found: Br, 48.36 and 48.29; C, 29.13 and 28.87; H, 3.49 and 3.12.

Dibromocyclohexantetrol, crystallizes from water in massive colorless prisms, melting at 216° with decomposition. It separates from hot ethyl acetate in small, shining prisms, and from alcohol in tufted crystals. It is soluble in benzene, chloroform, ether and amyl acetate. It is optically inactive.

Calc. for $C_6H_6Br_2(OH)_4$: Br, 59.29%; C, 23.53%; H, 3.27%. Found: Br, 59.29; C, 23.28; H, 3.35.

On acetylation, dibromocyclohexantetrol yields β -dibromotetracetylcyclohexantetrol.

It was found that four of the products prepared from acetyl bromide and inosite were identical with those obtained by Müller.² Since his method of procedure yielded a smaller number of esters, and since he mentions melting points for some of these compounds which are different from those observed in this laboratory, this part of his work was repeated.

Six grams of anhydrous hexacetylcyclohexanhexol and 20 g. of glacial acetic acid, saturated at 0° with hydrogen bromide, were heated in a sealed tube for 8 hours at 100° , and 8 hours at 150° . No pressure was noticed in opening the tube. The contents were divided into two portions. The products of one portion were separated according to the method of Müller, and the other, by the scheme adopted for acetyl bromide and inosite. Half the contents of the tube were emptied into water and the products which separated gradually solidified as a crystalline mass. This was extracted with cold alcohol which dissolved part of it. The insoluble residue was filtered off and the filtrate added to the water soluble portion. This mixture was evaporated in a vacuum to a thick syrup, water added, and boiled till solution took place. The clear liquid was concentrated and after standing in the ice box a few days a white powder separated. This was dried on porous plates and recrystallized from alcohol and finally from water, yielding large colorless prisms of dibromocyclohexantetrol, m. p. 216° .

¹ Correction made for halogen which was also saponified by the action of the sodium hydroxide.

² *J. Chem. Soc.*, 91, 1780 (1907).

The insoluble residue was a mixture of products which, by repeated crystallization from alcohol, were obtained pure. The small, indistinct crystals separating first were bromopentacetylcyclohexanpentol, m. p. 240° . These were followed by scaly crystals of α -dibromotetracetylcyclohexantetrol, m. p. 225° (Müller, m. p. 235°) and then massive rhombic prisms of β -dibromotetracetylcyclohexantetrol, m. p. 130° . (Müller, m. p. 140° .) From the alcoholic mother liquors two kinds of crystals were obtained. They were mechanically separated and each recrystallized from alcohol; one, massive prisms of β -dibromotetracetylcyclohexantetrol, m. p. 130° , and the other, soft, white needles of dibromodiacetylcyclohexantetrol, m. p. 214° . The latter substance is similar in properties to one observed by Müller, but not isolated by him. Müller, by hydrolysis of the mother liquors resulting from the separation of the above-mentioned products, obtained bromocyclohexanpentol. Neither by means of Müller's method, nor with acetyl bromide could any product like this be obtained.

The second half of the reaction mixture was treated as in the scheme for the separation of the products formed by the action of acetyl bromide and inosite, *i. e.*, direct evaporation in a vacuum and fractional crystallization from alcohol. Bromopentacetylcyclohexanpentol, m. p. 240° , separated first; followed by α -dibromotetracetylcyclohexantetrol, m. p. 225° , and then β -dibromotetracetylcyclohexantetrol, m. p. 130° , and finally dibromodiacetylcyclohexantetrol, m. p. 214° . The dark red mother liquors after long standing over calcium chloride yielded dibromocyclohexantetrol, m. p. 216° . (Müller, m. p. 210° .) The presence of tribromotriacetylcyclohexantriol or bromocyclohexanpentol was not observed.

This latter scheme of separating the products gave better yields than Müller's method.

Heating inosite with acetyl bromide in a sealed tube above 120° for a longer period than 6 hours had some effect on the amount of the products formed. When the reaction was carried out at 150° for 8 hours, none of the bromopentacetylcyclohexanpentol, but more of the tribromotriacetylcyclohexantriol was obtained. The formation of a tetra-halide ester of inosite at even higher temperatures was not successful since carbonization took place above 160° .

Besides the synthesis of these halogen esters of inosite some of their properties were studied to ascertain their behavior towards certain reagents. It was found that they were not affected by anhydrous aluminium chloride and dry benzene, nor by metallic sodium and ethyl bromide in ether, and only slightly affected by silver carbonate after long boiling in absolute methyl alcohol. Phenyl magnesium bromide in ether gave as final products, dark-colored resinous substances which were not identified, due to lack of material. It was hoped that by means of liquid ammonia, a halo-

gen in dibromotetracetylcyclohexantetrol might be replaced by an amino group. The products of the reaction showed that saponification of the acetyl groups had taken place, since only dibromocyclohexantetrol was obtained. However, the reaction was not given a fair trial, since large amounts of impurities such as water, iron, pyridine, etc., were subsequently found to be present in the liquid ammonia.

Five grams of β -dibromotetracetylcyclohexantetrol were mixed with liquid ammonia in a thermos bottle. After standing 12 hours, the contents were emptied into a flask to evaporate off the ammonia. The resulting dark-colored residue was extracted first with cold alcohol and then with water. The water solution yielded 1 g. of dibromocyclohexantetrol, while from the alcohol solution, after boiling with animal charcoal, was obtained 2 g. of unchanged β -dibromotetracetylcyclohexantetrol.

Action of Acetyl Chloride on Inosite.

When H. Müller,¹ heated hexacetylcyclohexanhexol with glacial acetic acid saturated with hydrogen chloride he obtained several monochloro esters of inosite, together with two new isomeric inosites, which he called iso and ψ .

By using acetyl chloride none of the above products seemed to be formed, but, as was to be expected, chloro esters of inosite were obtained similar in properties to those resulting from the action of acetyl bromide. Furthermore, these chloro esters of inosite appear to be isomorphous with the analogous bromo esters, since the latter served in inoculating the solutions from which the former were crystallized.

Twenty grams of inosite (dried at 110°) and 80 g. of acetyl chloride were heated in a sealed tube at 140° for 6 hours. Care was taken in opening the tube to prevent loss of the contents, due to frothing. The syrup obtained was emptied into a flask together with the pieces of the crushed glass tube. Absolute alcohol was added and the mixture evaporated in a vacuum on a water bath. The dark brown syrupy residue was dissolved in 500 cc. of hot alcohol and filtered hot. After cooling, the crystalline product (A) which separated was filtered and the filtrate evaporated to half its volume, with a current of air. A second crystalline product (B) resulted and the filtrate evaporated as before until an oil began to form, giving a white precipitate (C). The reddish black solution was heated with animal charcoal yielding a pale yellow solution which did not crystallize. Instead, a syrup slowly separated which dissolved on heating, but formed again on cooling. The mixture was evaporated to a syrup (D) in a vacuum and dried over calcium chloride. This syrup weighed 32 g. or 80% of the total yield obtained.

(A), (B), and (C) were mixtures and were separated by fractional crystallization from alcohol. (A) gave chloropentacetylcyclohexantetrol and α -dichlorotetracetylcyclohexantetrol while (B) yielded α - and β -dichlorotetracetylcyclohexantetrols. From (C), by mechanical separation, β -dichlorotetracetylcyclohexantetrol and a minute amount of white needles melting at 107° were obtained. The latter substance is probably dichlorodiacetylcyclohexantetrol, since its properties are similar to those of dibromodiacetylcyclohexantetrol. Furthermore, like the latter sub-

¹ *J. Chem. Soc.*, 101, 2383 (1912).

stance, it gave on acetylation the corresponding β -dichlorotetracetyl derivative. The syrup (D) was dichlorotriacetylcyclohexantetrol, which on hydrolysis with HCl gave dichlorocyclohexantetrol.

Chloropentacetylcyclohexanpentol crystallizes from hot alcohol in fine, indistinct crystals melting at 250° . It is soluble in benzene, chloroform and ether, and insoluble in water. It is optically inactive.

Calc. for $C_6H_6Cl(OCOCH_3)_5$: Cl, 8.70%; C, 47.00%; H, 5.14%. Found: Cl, 8.65; C, 46.87; H, 5.09.

α -Dichlorotetracetylcyclohexantetrol differs from its isomer in its crystalline form and is less soluble. It crystallizes from alcohol in shining scales, melting at 186° to a colorless liquid, which forms a crystalline mass on cooling. It is soluble in alcohol, chloroform, ethyl acetate, glacial acetic acid, benzene, ether and acetone, and insoluble in water and in ligroin. It is optically inactive.

Calc. for $C_6H_6Cl_2(OCOCH_3)_4$: Cl, 18.44%; C, 43.68%; H, 4.67%. Found: Cl, 18.37 and 18.25; C, 43.68; H, 4.75.

β -Dichlorotetracetylcyclohexantetrol crystallizes from alcohol in large, brilliant, rhombic prisms melting sharply at 118° . It is optically inactive.

Calc. for $C_6H_6Cl_2(OCOCH_3)_4$: Cl, 18.44%; C, 43.68%; H, 4.67%. Found: Cl, 18.42 and 18.50; C, 43.51; H, 4.60.

Dichlorotriacetylcyclohexantetrol distils at $216-217^{\circ}$ at 2.3 mm. It is a colorless, brittle gum, soluble in alcohol, glacial acetic acid, ethyl acetate and hot water. For analysis, small portions were dried to a constant weight at 80° in a vacuum over sulfuric acid. It is optically inactive.

Calc. for $C_6H_6Cl_3(OH)(OCOCH_3)_3$: Cl, 20.70%; C, 41.91%; H, 4.67%; Acetyl, 50.00%. Found: Cl, 20.73 and 20.78; C, 41.75; H, 4.14; Ac, 50.13 and 50.05.

On acetylation with acetic anhydride β -dichlorotetracetylcyclohexantetrol, was formed. Dichlorotriacetylcyclohexantetrol in an alcoholic solution was hydrolyzed for 12 hours with hydrochloric acid. The chlorides were removed with silver carbonate, and the solution boiled with bone black, filtered and evaporated to a syrupy consistency. On inoculating with a crystal of dibromocyclohexantetrol and vigorously agitating the mixture, a crystalline mass of dichlorocyclohexantetrol separated. This was filtered, washed with ethyl acetate and recrystallized from alcohol. On acetylation, it gave β -dichlorotetracetylcyclohexantetrol.

Dichlorocyclohexantetrol crystallizes from alcohol in small, colorless prisms, melting at 221° . It is soluble in water and in alcohol; less soluble in ethyl acetate and insoluble in chloroform, ether and benzene.

Calc. for $C_6H_6Cl_2(OH)_4$: Cl, 32.72%; C, 33.18%; H, 4.61%. Found: Cl, 32.62; C, 33.30; H, 4.77.

Maquenne¹ prepared hexacetyl and hexabenzoylcyclohexanhexol by

¹ *Compt. rend.*, 104, 297 (1887).

means of the acid chlorides. This suggested that other acyl derivatives of inosite might be obtained by employing other acid chlorides.

The method adopted was to mix powdered anhydrous inosite with quinoline in slight excess of that necessary to react with the calculated amount of acid chloride. The mixture was heated at 120° till solution was complete, usually half an hour. The resulting syrupy mass was dissolved in 100 cc. of chloroform and washed two or three times with dilute sulfuric acid. The pale yellow solution was concentrated to about 25 cc. and warm alcohol added to the point of precipitation. The products separated on cooling and were usually purified by fractional crystallization.

Hexa-, penta-, and tetra-acyl derivatives of inosite were thus obtained. The hexacyl derivatives were less soluble and the melting points lower than the corresponding pentacyl derivatives.

Benzoylation of Inosite.—Maquenne¹ by direct heating of inosite with benzoyl chloride and zinc chloride obtained hexabenzoylcyclohexanhexol and chlorotribenzoylcyclohexanpentol. By using quinoline, no chloro esters were obtained, but instead lower benzoyl derivatives of inosite.

Two grams of inosite, 10 g. of quinoline and 10 g. of benzoyl chloride were heated in a flask for half an hour at 120° . The orange red syrup obtained was dissolved in 100 cc. of chloroform and washed two or three times with 10% sulfuric acid, and then once with water. The light yellow solution was evaporated to 25 cc. and 100 cc. of alcohol added. A white crystalline precipitate of pentabenzoylcyclohexanhexol separated. The filtrate was concentrated to 50 cc. After standing in the ice box for 12 hours, 4 g. of hexabenzoylcyclohexanhexol were obtained in the form of crystals. When the alcoholic mother liquors were poured into water, a small amount of an amorphous product separated and proved to be the tetrabenzoyl derivative. They were obtained pure by recrystallization from other solvents.

Hexabenzoylcyclohexanhexol crystallizes from hot alcohol in microscopic crystals, m. p. 258° . It is soluble in benzene, glacial acetic acid and chloroform, slightly soluble in alcohol or ether, and insoluble in water.

Calc. for $C_6H_6(OCOC_6H_5)_6$: C, 71.64%; H, 4.34%. Found: C, 71.41; H, 4.42.

Pentabenzoylcyclohexanhexol crystallizes from benzene in large transparent prisms, m. p. 269° . It is soluble in chloroform, acetone, ethyl acetate, glacial acetic acid, and in benzene, insoluble in water, ligroin and in ether.

Calc. for $C_6H_6(OH)(OCOC_6H_5)_5$: C, 70.29%; H, 4.57%. Found: C, 70.39 and 70.29; H, 4.68 and 4.71.

Tetrabenzoylcyclohexanhexol separates from a mixture of chloroform and alcohol as a white amorphous powder, m. p. 231° .

Calc. for $C_6H_6(OH)_2(OCOC_6H_5)_4$: C, 68.46%; H, 4.69%. Found: C, 68.41; H, 4.55.

Anisylation of Inosite.—Two grams of dry inosite, 20 g. of quinoline and 11.5 g. of anisyl chloride were mixed in a flask and heated for half an hour at 120° . The resulting pale brown syrup was dissolved in 100 cc. of chloroform and washed twice with 10% sulfuric acid, and once with water. The yellow solution was concentrated to 25 cc. and 50 cc. of hot alcohol added. On cooling, a mixture of hexa- and pentanisyl-

¹ *Loc. cit.*

cyclohexanhexol separated, and was dried on a porous plate. This crude product amounted to 7 g. It was dissolved in a hot mixture of equal volumes of chloroform and alcohol, which gave on cooling hexanisylcyclohexanhexol. From the mother liquors pentanisylcyclohexanhexol was obtained.

The hexanisyl derivative crystallizes from a mixture of equal volumes of chloroform and alcohol in fine, white prisms, melting at 225° . It is soluble in chloroform, difficultly soluble in acetone or in ethyl acetate, and insoluble in alcohol, ether, benzene or in water. It is optically inactive.

Calc. for $C_6H_5(OCOC_6H_4OCH_3)_6$: C, 65.86%; H, 4.88%. Found: C, 65.81 and 66.09; H, 5.15 and 4.94.

The pentanisyl derivative crystallizes from a mixture of chloroform and alcohol in microscopic needles, melting at 251° . It is soluble in chloroform, less so in acetone, and insoluble in alcohol, water or in ether.

Calc. for $C_6H_5(OH)(OCOC_6H_4OCH_3)_5$: C, 64.94%; H, 4.94%. Found: C, 64.80 and 64.93; H, 4.80 and 5.01.

Cinnamoylation of Inosite.—Two grams of anhydrous inosite, 20 g. of quinoline, and 12 g. of cinnamoyl chloride (prepared by distilling a solution of cinnamic acid and phosphorus trichloride in a vacuum of 21 mm. at 145°), were mixed in a flask and heated for half an hour at 120° . The resulting orange-red syrup was dissolved in 100 cc. of chloroform and washed three times with 10% sulfuric acid and once with water. The pale yellow chloroform solution was concentrated to 25 cc. and hot alcohol was added till a turbidity formed. On cooling an amorphous product separated. 200 cc. of alcohol were added and the mixture set away in the ice box for 12 hours. The resulting mixture was filtered. The residue was dried on a porous plate giving 6 g. of a white powder. It consisted of two substances, hexa- and α -pentacinnamoylcyclohexanhexol, which were separated by fractional crystallization from a mixture of equal volumes of chloroform and alcohol. A third product, β -pentacinnamoylcyclohexanhexol, was obtained from the mother liquors in the form of an amorphous product contaminated with a syrup. It was purified by pressing out on porous plates and crystallizing from hot alcohol.

The hexacinnamoyl compound crystallizes from a mixture of chloroform and alcohol in clusters of fine needles, m. p. 199° . It is soluble in chloroform or in acetone, and insoluble in water, ether, alcohol, or in benzene.

Calc. for $C_6H_5(OCOC_3H_3C_6H_5)_6$: C, 75.20%; H, 5.00%. Found: C, 75.19 and 75.20; H, 5.32 and 5.31.

The α -pentacinnamoyl derivative crystallizes from chloroform and alcohol in microscopic prisms, m. p. 271° . It is soluble in chloroform or in acetone, and insoluble in water, ether, alcohol, or in benzene. It is optically inactive.

Calc. for $C_6H_5(OH)(OCOC_3H_3C_6H_5)_5$: C, 73.73%; H, 5.06%. Found: C, 73.58 and 73.50; H, 5.18 and 5.06.

The β -pentacinnamoyl derivative is a white, amorphous powder, m. p. 125° . It is soluble in chloroform, benzene or in alcohol, and insoluble in methyl alcohol, ether or in water.

Calculated for $C_6H_8(OH)(OCOC_2H_5C_6H_5)_2$: C, 73.73%; H, 5.06%. Found: C, 73.58; H, 5.16.

***m* Nitrobenzoylation of Inosite.**—Two grams of anhydrous inosite, 18 g. of quinine and 14 g. of metanitrobenzoyl chloride were dissolved by heating at 120° for half hour. The resulting pale brown solution was taken up in 100 cc. of chloroform and washed two or three times with dilute sulfuric acid and once with water. The solution was concentrated to 40 cc. and 10 cc. of hot alcohol added. On cooling, a red syrup separated which changed to a crystalline mass on standing in the ice box over night. The mass was dried on porous plates, pulverized, and the color removed by boiling with alcohol. Eight grams of hexa-*m*-nitrobenzoylcyclohexanhexol were obtained in the form of an insoluble, white powder. The mother liquors gave a small amount of penta-*m*-nitrobenzoylcyclohexanhexol.

The penta-*m*-nitrobenzoyl derivative separates as a white powder from amyl alcohol, m. p. 226° . It is soluble in chloroform or in acetone, and insoluble in water, alcohol, ligroin, or in ether.

Calc. for $C_6H_8(OH)(OCOC_2H_4NO_2)_2$: C, 53.19%; H, 2.92%. Found: C, 53.00; H, 2.75.

The hexa-*m*-nitrobenzoyl compound crystallizes from ethyl acetate in fine, shining needles, m. p. 217° . It is soluble in chloroform or in acetone; slightly soluble in ethyl acetate or in benzene; and insoluble in water, ether, or in alcohol.

Calc. for $C_6H_8(OCOC_2H_4NO_2)_2$: C, 53.63%; H, 2.80%. Found: C, 53.81 and 53.75; H, 3.02 and 2.77.

Action of Chlorocarbonic Acid Ester on Inosite.—Carbonates of inosite are probably formed by heating inosite with chlorocarbonic acid ester and quinine, and are insoluble in anhydrous solvents. The product obtained is a hygroscopic syrup soluble in alcohol but at the same time inosite is formed. This may be due to alcoholysis having taken place. Acetylation of the syrup yields a mixture of two isomeric hexacetylcyclohexanhexols, which were named α and β , and which are both different from the hexacetylcyclohexanhexol, obtained by direct acetylation of inosite.

Two grams of finely pulverized anhydrous inosite were thoroughly mixed with 10 g. of quinine. Eight grams of chlorocarbonic acid ethyl ester were slowly added, keeping the mixture cold. After the frothing had ceased, the mixture was warmed until complete solution had taken place. The resulting dark-colored syrup was extracted with hot chloroform to remove the coloring material. After decanting off the chloroform, a white, hygroscopic syrup remained which was kept in a desiccator over sulfuric acid. The syrup was dissolved in acetic anhydride containing two drops of sulfuric acid, and the solution poured into water, from which an oil separated which gradually solidified. The white, amorphous mass thus obtained was washed with water and dissolved in hot alcohol. On cooling, a crystalline mass consisting of two acetylated products separated. By fractional crystallization from alcohol the α -hexacetylcyclohexanhexol was obtained, followed by the β -hexacetylcyclohexanhexol.

To determine the acetyl number a weighed amount (0.15–0.20 g.) was dissolved in 35 cc. of methyl alcohol in a flask connected with a ground-in reflux condenser, surmounted by a bent tube filled with soda lime. Thirty cubic centimeters of 0.1 *N*

sodium hydroxide were added and the solution warmed on the water bath for 2 hours—5 hours for substances containing halogen—and titrated with 0.1 *N* hydrochloric acid, using phenolphthalein as an indicator.

α -Hexacetylcyclohexanhexol crystallizes from alcohol in small, flat prisms melting sharply at 212° . It is soluble in chloroform, benzene and in glacial acetic acid; less soluble in ether and in methyl alcohol, and insoluble in water. It is optically inactive. On hydrolysis with methyl alcohol and sodium hydroxide it yielded inosite.

Calc. for $C_6H_6(OCOCH_3)_6$: C, 50.00%; H, 5.55%; Ac, 81.94%. Found: C, 50.06 and 50.01; H, 5.56 and 5.72; Ac, 81.73 and 81.80.

β -Hexacetylcyclohexanhexol crystallizes from alcohol in microscopic prisms melting at 200° . It is soluble in ether, benzene, chloroform and in glacial acetic acid, and insoluble in water or in ligroin. It is optically inactive. On hydrolysis with methyl alcohol and sodium hydroxide it yielded inosite.

Calc. for $C_6H_6(OCOCH_3)_6$: C, 50.00%; H, 5.55%; Ac, 81.94%. Found: C 50.03 and 50.15; H, 5.68 and 5.79; Ac, 82.17 and 81.90.

On one occasion, α -hexacetylcyclohexanhexol changed over to β -hexacetylcyclohexanhexol. This interesting transformation could not be repeated although several attempts were made.

In order to study the relation of hexacetylcyclohexanhexol to α - and β -hexacetylcyclohexanhexols, it was warmed with quinoline and chloro-carbonic acid ester but no change took place. Also, it remained unchanged when treated with acetic anhydride saturated with hydrogen chloride.

It is stated by Fick¹ that a pentacetate, m. p. 216° , and a tetracetate have been obtained on short heating of inosite with acetic anhydride. In repeating the work, hexacetylcyclohexanhexol, m. p. 126° , was the only crystalline body obtained. The mother liquors gave a syrup, probably lower acetyl derivatives.

Lower acetyl derivatives of inosite in the form of syrups and the hexacetyl derivatives, m. p. 212° , were obtained by Maquenne,² on heating inosite with acetyl chloride. The work was repeated by the same method used for the formation of acyl derivatives in the presence of quinoline as mentioned above. A poor yield of hexacetylcyclohexanhexol, in addition to a small amount of a hygroscopic syrup, was obtained. This syrup is probably a lower acetylated derivative, since it is soluble in chloroform and in alcohol, and insoluble in water. Being unimportant, it was not investigated.

Hexacetylcyclohexanhexol crystallizes from toluene in monoclinic prisms, melting sharply at 216° , to a clear, colorless liquid, which solidifies on cooling. It sublimates at 200° and boils in a vacuum (2.5 mm.)

¹ *Chem. Zentr.*, 1887, 452.

² *Bull. soc. chim.*, 48, 58 (1887).

at 234°. Saponification with liquid ammonia or with boiling alcoholic barium hydroxide gives inosite.

Calc. for $C_6H_8(OCOCH_3)_4$: C, 50.00%; H, 5.55%. Found: C, 50.04; H, 5.64.

Action of Liquid Ammonia on Hexacetylcyclohexanhexol.—The replacement of the acetyl groups with amino groups by means of liquid ammonia was undertaken. Only saponification of the acetyl groups took place with the production of inosite.

In a thermos bottle containing 50 cc. of liquid ammonia, 5 g. of the dry finely powdered compound were slowly added with stirring. After standing for 12 hours, the contents of the thermos bottle were emptied into a short-necked flask, the ammonia evaporating in about two hours. A brown residue resulted, which was extracted with alcohol. The alcohol solution gave a small amount of unchanged substance, but no intermediate acetylated derivatives could be obtained. The residue was dissolved in water, boiled with animal charcoal, and filtered. The filtrate was evaporated to 5 cc. and 30 cc. of alcohol added. The crystalline precipitate which formed was recrystallized from hot 80% alcohol, yielding 2 g. of inosite, m. p. 225°.

Alkylation of Inosite.

The occurrence of methyl ethers of inosite in nature suggested the alkylation of inosite. Of the many reagents employed for the alkylation of hydroxyl groups, dialkyl sulfate and a hot, 25% solution of sodium hydroxide was the only one which proved successful in the alkylation of inosite. The alkyl inosites obtained were of course optically inactive, and therefore it is impossible to say whether they are identical with the natural ethers which are active.

Unchanged inosite was obtained from heating inosite with diazomethane; a 15% alcohol solution of potassium hydroxide and methyl iodide; silver oxide, methyl alcohol, and methyl iodide, and also in a sealed tube; absolute methyl alcohol and hydrogen chloride in a sealed tube; and dimethyl sulfate with quinoline, and with pyridine.

Methylation of Inosite.—Ten grams of inosite were dissolved in 130 cc. of a 25% sodium hydroxide solution, heated to boiling, and 50 g. of dimethyl sulfate slowly added. The mixture was boiled for 24 hours, neutralized with a few drops of sulfuric acid and diluted with water. It was boiled with an excess of barium hydroxide, cooled, filtered, and the excess of barium hydroxide removed with carbon dioxide. The resulting pale yellow solution was acidified with acetic acid and boiled.

Any unchanged inosite was separated as the lead salt, $2C_6H_{12}O_6 \cdot 5PbO$, by making the solution ammoniacal and then adding 50 cc. of a saturated solution of basic lead acetate, followed by 50 cc. of methyl alcohol. The addition of the alcohol causes the gelatinous mass to settle as a fine, white precipitate which is more easily filtered. The lead salts were decomposed with hydrogen sulfide and the resulting solution evaporated to 10 cc. Upon the addition of alcohol, 3 g. of inosite were obtained.

The lead salts in the original filtrate were precipitated with hydrogen sulfide. After boiling off the hydrogen sulfide the filtrate was concentrated on the water bath to a syrupy consistency. The syrupy mass was dried at 100° in a vacuum over sulfuric acid. The resulting hard, hygroscopic product was pulverized, emptied into 100 cc. of acetic anhydride, containing a few drops of sulfuric acid, and the mixture heated for an hour. After cooling, the mixture was filtered. The dark red solution was evap-

orated to a syrup, dissolved in alcohol and evaporated a second time. The syrupy residue was extracted with chloroform, filtered, and the chloroform distilled off. The dark-colored syrup thus obtained was dissolved in alcohol, boiled with animal charcoal, and filtered. The solution was evaporated to a pale yellow syrup, extracted with ether, and decanted from the tetracetyldimethylcyclohexanhexol which remained undissolved. From the ethereal solution, silky needles of pentacetylmethylcyclohexanhexol slowly separated. The mother liquors gave a yellow syrup, triacetyldimethylcyclohexanhexol, which was equal to 70–80% of the total yield obtained. Monomethylcyclohexanhexol was prepared by heating 2 g. of pentacetylmethylcyclohexanhexol with an aqueous solution containing 4 g. barium hydroxide. A slight excess of sulfuric acid was added and the mixture filtered. The filtrate was concentrated to a syrupy consistency and absolute alcohol added with stirring. A small amount of monomethylcyclohexanhexol separated as a white, amorphous mass. The alcoholic filtrate yielded a syrupy, optically inactive and which has not been identified.

Monomethylcyclohexanhexol crystallizes from hot alcohol in microscopic prisms, melting at 204° . It is soluble in water, less soluble in alcohol and insoluble in ether.

Calc. for $C_8H_{16}OCH_2(OH)_1$: C, 43.30%; H, 7.22%. Found: C, 43.42; H, 7.38.

Pentacetylmethylcyclohexanhexol, crystallizes from ether in long, white needles, melting at 141° . It is soluble in alcohol, benzene, glacial acetic acid, chloroform, and ethyl acetate. The crystals when exposed to the air for some time take up one and one-half molecules of water, and then melt at 96° . In a vacuum over sulfuric acid they lose this water and melt at 141° . It is optically inactive.

Calc. for $C_8H_{16}OCH_2(OCOCH_3)_5 + 1\frac{1}{2}H_2O$: $H_2O = 6.26\%$; 0.6789 g. subs. lost 0.0422 g. of water = 6.22%.

Calc. for $C_8H_{16}OCH_2(OCOCH_3)_5$: C, 50.49%; H, 5.94%; Ac, 73.02%. Found: C, 50.52 and 50.47; H, 6.10 and 6.01; Ac, 73.01 and 72.88.

Tetracetyldimethylcyclohexanhexol, crystallizes from alcohol in small prisms, which melt at 223° and sublime unchanged above 300° . It is soluble in benzene, chloroform, alcohol, ethyl acetate and acetone, difficultly soluble in ether, and insoluble in water and in ligroin.

Calculated for $C_8H_{16}(OCH_2)_2(OCOCH_3)_4$: C, 51.06%; H, 6.38%; Ac, 62.77%. Found: C, 51.05 and 50.93; H, 6.38 and 6.31; Ac, 62.45 and 62.52.

On hydrolysis with an alcoholic solution of barium hydroxide, a syrup soluble in water was obtained which is probably a dimethylcyclohexanhexol.

Triacetyldimethylcyclohexanhexol is a syrup which could not be crystallized. It distils at $212-213^{\circ}$, and 2.5 mm. pressure. It is soluble in alcohol, acetone, ethyl acetate and glacial acetic acid; slightly soluble in hot water. Portions for analysis were dried to constant weight in a vacuum over sulfuric acid at 100° .

Calculated for $C_8H_{16}(OCH_2)_2OH(OCOCH_3)_3$: C, 50.30%; H, 6.56%; Ac, 53.00%. Found: C, 50.48 and 50.34; H, 6.59 and 6.64; Ac, 52.85 and 52.73.

On hydrolysis with barium hydroxide solution, an unidentified syrup was obtained which will be further investigated.

Ethylation of Inosite.—Thirty-five grams of diethyl sulfate were slowly dropped into a boiling solution of 10 g. of inosite and 70 cc. of 25% sodium hydroxide. The boiling was continued for 48 hours and the sodium sulfate which separated was filtered off. The yellow solution was concentrated to a thick paste on the water bath and then dried in a vacuum over sulfuric acid at 100°. The resulting hygroscopic mass was pulverized and emptied into a flask containing 50 cc. of acetic anhydride and 2 drops of sulfuric acid. The mixture was heated for an hour, cooled and filtered. The filtrate was evaporated to a syrup, dissolved in alcohol and again evaporated. The syrupy mass was extracted with chloroform and the chloroform distilled off. The dark-colored syrup thus obtained was dissolved in alcohol, boiled with animal charcoal and filtered. The resulting pale yellow solution was evaporated to a syrup and dissolved in boiling ether. On cooling, small prisms of tetracetyldiethylcyclohexanhexol separated. As the ether gradually evaporated, soft, white needles of pentacetylethylcyclohexanhexol crystallized. The mother liquors gave a syrup equal to 70–80% of the total yield. This pale yellow syrup on hydrolysis yielded another syrup which has not been identified.

Pentacetylethylcyclohexanhexol crystallizes from ether in long, white needles melting at 128°. It is soluble in chloroform, alcohol, glacial acetic acid, acetone and in benzene. It is optically inactive.

Calc. for $C_6H_6(OC_2H_5)_5(OCOCH_3)_1$: C, 51.67%; H, 6.22%; Ac, 70.58%. Found: C, 51.54 and 51.60; H, 6.19 and 6.04; Ac, 70.41 and 70.46.

Tetracetyldiethylcyclohexanhexol crystallizes from alcohol in small prisms melting at 212°, and subliming unchanged above 300°. It is soluble in benzene, chloroform, acetone, and in ethyl acetate, slightly soluble in ether, and insoluble in ligroin or in water. It is optically inactive.

Calc. for $C_6H_6(OC_2H_5)_4(OCOCH_3)_2$: C, 53.46%; H, 6.94%; Ac, 58.42%. Found: C, 53.48 and 53.46; H, 7.01 and 6.93; Ac, 58.31 and 58.65.

An alcoholic solution of tetracetyldiethylcyclohexanhexol was heated with a slight excess of barium hydroxide, sulfuric acid added, and the solution concentrated to a thick syrup. Absolute alcohol was added and on agitating the mixture, diethylcyclohexanhexol was separated.

Diethylcyclohexanhexol crystallizes from hot alcohol in small, shining prisms, which melt at 212°. It is soluble in water and insoluble in ether or in benzene.

Calculated for $C_6H_6(OC_2H_5)_2(OH)_4$: C, 50.67%; H, 8.69%. Found: C, 50.78; H, 8.67.

Derivatives of Pinite.

Preparation of Pinite.—Pinite is obtained from the roots of the "Pinus Lambertina," a species of Californian pine tree, in the form of a dark-colored granular substance with an aromatic odor, mixed with resinous material and pine needles. It was purified in the following manner:

One hundred grams of the crude pinite were dissolved in 250 cc. of water and the volatile resins distilled with steam. The solution was evaporated to a syrupy consistency, dissolved in warm alcohol and filtered. The dark-red filtrate was transferred to a bowl and set away in the ice box. Crystals,

which adhered tenaciously to the sides of the bowl, separated. They were pulverized, dried on porous plates and recrystallized from hot alcohol. After remaining in the ice box for several weeks, another crop of crystals was obtained from the black mother liquors. A total yield of 71 g. of pinite was obtained. It gave the Scherer test.

Pinite, monomethylcyclohexanhexol, $C_6H_6OCH_3(OH)_5$, crystallizes from methyl alcohol in small, white prisms, which melt sharply at 186° . It sublimes unchanged above 200° giving fine, colorless needles. It crystallizes from water with difficulty. It is insoluble in absolute alcohol or in ether. The optical rotation was determined by dissolving 0.6950 g. of the anhydrous substance in 100 cc. of water, from which the air had been expelled. This gave $[\alpha]_D^{25} = +65.3^\circ$. This rotation approaches nearest $[\alpha]_D^{22} = +65.5^\circ$, the value determined by Maquenne.¹ Other investigators give² $[\alpha]_D^{20} = +65.0^\circ$; and³ $[\alpha]_D^{20} = +65.7^\circ$.

Previous to this investigation, no crystalline acyl derivatives of pinite had been prepared. The acetyl and benzoyl derivatives were obtained by direct heating with the acid chloride, while the anisyl and cinnamoyl ethers required the presence of quinoline.

Acetylation of Pinite.—Maquenne⁴ obtained, on heating pinite with acetic anhydride and zinc chloride, a white, amorphous mass which he called pinite acetate. The work was repeated, and the amorphous mass obtained, which however could not be crystallized. A crystalline pentacetyl derivative of pinite was finally prepared by employing acetyl bromide.

Three grams of pulverized pinite (dried at 110°) and 15 g. of acetyl bromide were placed in a round-bottomed flask connected with a long ground-in glass tube, and gently warmed for half an hour. Hydrogen bromide was given off as the pinite slowly dissolved. The reddish yellow solution was emptied into cold water and settled as an oil, which gradually turned to a white syrup. The syrup was dissolved in alcohol and hot water added till a turbidity formed. On cooling, a fine, white precipitate separated and was filtered. It was recrystallized from 80% methyl alcohol, giving 5 g. of pentacetylmethylcyclohexanhexol.

Pentacetylmethylcyclohexanhexol crystallizes from 80% alcohol in clusters of fine prisms, melting at 98° to a clear liquid. It is insoluble in water, but readily soluble in alcohol, methyl alcohol, glacial acetic acid, benzene, ether, chloroform, acetone and ethyl acetate, $[\alpha]_D^{20} = -9.67^\circ$.

Calc. for $C_6H_6OCH_3(OCOCH_3)_5$: C, 50.49%; H, 5.94%; Ac, 73.02%. Found: C, 50.50 and 50.41; H, 5.81 and 6.09; Ac, 73.30 and 73.11.

On hydrolysis with 50% methyl alcohol solution of barium hydroxide, pinite, m. p. 186° , was obtained.

¹ *Ann. chim. phys.*, [6] 22, 264 (1891).

² Seidel, Thesis des Dorpat.

³ Girard and Combes, *Compt. rend.*, 110, 84 (1890).

⁴ *Loc. cit.*

Benzoylation of Pinite.—Three grams of pulverized anhydrous pinite and 11 g. of benzoyl chloride were placed in a round-bottomed flask connected with a long ground-in glass tube, and heated to boiling for fifteen minutes. To the resulting pale brown solution water was added giving a gummy product. This mixture was heated for an hour, after which a hard, white mass separated out. The water was decanted off and the mass dissolved in boiling absolute alcohol and water added till a precipitate formed. On cooling, a gummy, white mass separated which was filtered off and dried on porous plates. The resulting hard mass was pulverized, dissolved in boiling 80% methyl alcohol and yielded, on cooling, 7 g. of a white, amorphous precipitate of pentabenzoylmethylcyclohexanhexol.

Pentabenzoylmethylcyclohexanhexol separates as a white, amorphous powder, m. p. 97° . It is soluble in alcohol, methyl alcohol, benzene, ether, chloroform, and in glacial acetic acid, and insoluble in water and in ligroin. $[\alpha]_D^{20} = +32.3^{\circ}$.

Calculated for $C_{36}H_{54}OCH_3(OCOC_6H_5)_5$: C, 70.59%; H, 4.76%. Found: C, 70.50 and 70.44; H, 4.76 and 4.73.

A methyl alcoholic solution of this compound was boiled for twenty-four hours with barium hydroxide. An excess of sulfuric acid was then added and the filtrate evaporated to nearly a syrup. On the addition of alcohol a precipitate of pinite, m. p. 186° , resulted.

Anisylation of Pinite.—Three grams of pinite, 11 g. of quinoline, and 13 g. of anisylchloride were heated in a flask for half an hour at 120° . The resulting pale brown solution was dissolved in 100 cc. of chloroform and washed two or three times with a 10% solution of sulfuric acid and once with water. The pale yellow chloroform solution was evaporated to 25 cc. and 100 cc. of hot alcohol added. On cooling, 4 g. of long, white needles of pentanisylmethylcyclohexanhexol crystallized.

Pentanisylmethylcyclohexanhexol crystallizes from alcohol in long, white needles, m. p. 101° . It is soluble in alcohol, methyl alcohol, glacial acetic acid, chloroform, and in benzene. It is insoluble in water. $[\alpha]_D^{20} = \pm 0.0^{\circ}$.

Calc. for $C_{36}H_{54}OCH_3(OCOC_6H_4OCH_3)_5$: C, 65.29%; H, 5.09%. Found: C, 65.29 and 65.19; H, 4.93 and 5.06.

Cinnamoylation of Pinite.—Three grams of pinite, 12 g. of quinoline, and 12 g. of cinnamoyl chloride were heated together for half an hour at 120° . The dark orange-colored syrup was dissolved in 100 cc. of chloroform and washed three times with 10% sulfuric acid and once with water. The pale yellow chloroform solution was concentrated to 25 cc. and 100 cc. of alcohol added. On standing over night a yellow syrup settled, which was dissolved in the least amount of glacial acetic acid and then poured into 50% alcohol. Six grams of pentacinnamoylmethylcyclohexanhexol, in the form of a yellow, amorphous mass was obtained, which was purified by repeating the operation several times. A yield of 4.5 g. of the purified substance was finally obtained.

Pentacinnamoylmethylcyclohexanhexol slowly separates from hot absolute alcohol as a white, amorphous powder, m. p. 105° . It is soluble in benzene, chloroform, ethyl acetate, glacial acetic acid, and in acetone; slightly soluble in alcohol, and insoluble in water and in methyl alcohol. $[\alpha]_D^{20} = +41.2^{\circ}$.

Calc. for $C_6H_5OCH_2(OCOC_2H_5C_6H_5)_5$: C, 74.00%; H, 5.21%. Found: C, 74.13 and 74.06; H, 5.34 and 5.46.

Nitration of Pinite.—One gram of anhydrous pinite was dissolved in a mixture of 5 cc. of fuming nitric acid and 10 cc. of sulfuric acid. The colorless oil which separated was poured into water. The white syrup which gradually formed was purified by dissolving in alcohol and pouring into water. The syrup which separated was soluble in alcohol, methyl alcohol, ethyl and amyl acetates, acetone, ether, benzene, pyridine, chloroform, carbon disulfide and in glacial acetic acid, but did not crystallize. It was insoluble in ligroin and in water. It possessed a bitter taste, easily decomposed on heating, and exploded when struck with a hammer.

Action of Acetyl Bromide on Pinite.—By the action of acetyl bromide on pinite in a sealed tube, dibromo esters of inosite were obtained. This shows that the methoxy group was also effected by the acid bromide.

Five grams of pinite (dried at 110°) and 19 g. of acetyl bromide were placed in a sealed tube. After remaining 72 hours at room temperature, a dark red solution resulted. This was emptied into water and an oil separated which gradually solidified. The mass was filtered, dissolved in hot alcohol, and on cooling separated as a fine, crystalline substance. This proved to be a mixture, which was separated by fractional crystallization from alcohol. Scaly crystals of α -dibromotetracetylcyclohexantetrol and large prisms of β -dibromotetracetylcyclohexantetrol were obtained. The water solution obtained above was evaporated to 50 cc. and combined with the alcoholic mother liquors and the mixture boiled with animal charcoal for five hours. The resulting pale yellow solution was concentrated to 25 cc. and set away in the ice box over calcium chloride for several days. Colorless, prismatic crystals of dibromocyclohexantetrol, m. p. 216° , were obtained.

On analysis, α -dibromotetracetylcyclohexantetrol gave Br = 33.80%; calc. for $C_6H_4Br_2(OCOCH_3)_4$: 33.75%.

β -Bromotetracetyl glucose containing a trace of impurity readily decomposes. This was noticeable in the case of the halide esters of inosite but to a lesser extent.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA.]

TEMPERATURE COEFFICIENTS AND THE EFFECTS OF ACIDS, BASES AND SALTS IN REACTION VELOCITIES OF THE TRIPHENYLMETHANE DYES.

BY H. C. BIDDLE AND C. W. PORTER.

Received April 15, 1915.

1. Introduction.

The study of color changes among acid and basic derivatives of triphenylmethane has engaged the attention of many investigators.

As early as 1888 Nietzki¹ attributed a quinoid structure to the colored

¹ *Organische Farbstoffe*, 1888.

forms of triphenylmethane dyes. In 1892 Bernthsen¹ produced evidence that phenolphthalein derivatives have the lactone structure in their colorless forms and the quinoid arrangement in the colored modifications. K. H. Meyer and A. Hantzsch² have prepared double salts of quinoidal phenolphthalein with aluminum chloride and with stannic chloride. They studied the colors and absorption spectra of these components and in their opinion the colored form is invariably quinoidal. It is unnecessary to review the vast amount of work that has been done in establishing the nature of the dynamic isomerism of triphenylmethane derivatives. The fact that it consists of an establishment of equilibrium between benzoid and quinoid forms is generally recognized. The evidence upon which this conclusion is based has been critically examined by Stieglitz³ in his "Theory of Indicators," and a summary of the early researches in this field is included in Ley's "Farbe und Konstitution bei Organischen Verbindungen."⁴ An interpretation of tautomeric change based on the movement of an electron from one part of the molecule to another⁵ has also been suggested, in connection with an oscillatory shift in constitution, as a possible explanation of color in the case of the triphenylmethane dyes.⁶

Several investigators have studied the velocity of changes among dyes of the triphenylmethane series and related bodies. Hantzsch⁷ and others employed the variation in electrical conductance as a measure of the speed. Sidgwick⁸ and his co-workers used a colorimetric method in determining the speed of change in diamino derivatives of triphenylcarbinol in the presence of acids and bases. Biddle⁹ employed a similar method in studying the conversion of triamino derivatives from the colorless into the colored forms under the influence of varying concentrations of hydrogen ion. He also noted the influence of neutral salts upon the reaction and made a preliminary study of this effect. This was followed by a study of the rate of fading of crystal violet in acid solution by Adams and Rosenstein.¹⁰

As pointed out by Biddle,¹¹ the effect of varying the concentration of hydrogen ion upon crystal violet and related bodies is two-fold. One effect is instantaneous producing in the colored form a change of tint.

¹ *Chem. Ztg.*, 16, 1957 (1892).

² *Ber.*, 40, 3497 (1907).

³ *THIS JOURNAL*, 25, 1112 (1903).

⁴ Leipzig, 1911.

⁵ See Lewis, *THIS JOURNAL*, 35, 1448 (1913).

⁶ Adams and Rosenstein, *Ibid.*, 36, 1452 (1914).

⁷ Hantzsch and Kolb, *Ber.*, 32, 3109 (1899).

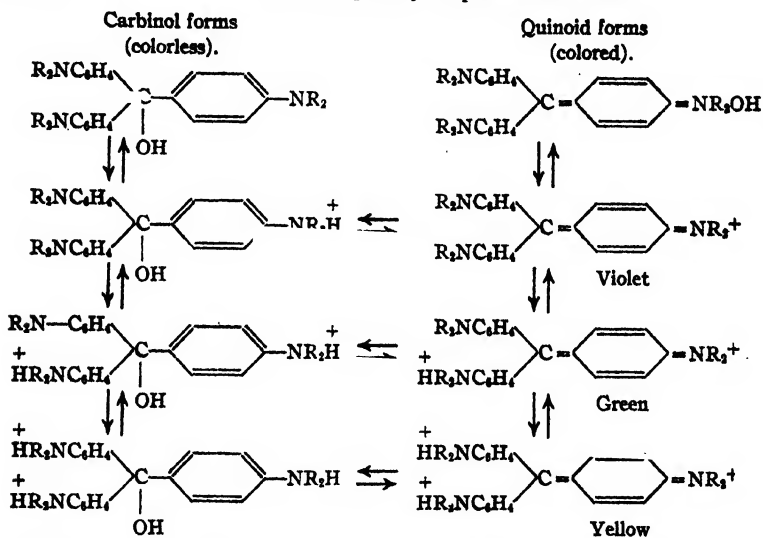
⁸ Sidgwick and Moore, *Z. physik. Chem.*, 58, 385 (1907) and *J. Chem. Soc.*, 95, 889 (1909); Sidgwick and Rivett, *Ibid.*, 95, 899 (1909).

⁹ *THIS JOURNAL*, 35, 273 (1913); 36, 84 (1914).

¹⁰ *Ibid.*, 36, 1454 (1914).

¹¹ *Ibid.*, 36, 85 (1914).

The other is a time reaction leading to an alteration in the intensity of the color. It was further indicated that any equilibrium between benzoid and quinoid forms involves equilibria between the mono-, di-, and tri-basic ions of the colored and colorless forms. This idea has been elaborated by Adams and Rosenstein¹ who, following the suggestions of Rosenstiehl,² assume the formation of a series of intermediate benzoid ions of the type $(R_2N-C_6H_4)_3C$. Since, as indicated by E. and O. Fischer,³ the conversion of carbinol ion to quinoid ion may take place directly by loss of water, it is simpler to represent the equilibrium as existing solely between these two types. The forms between which equilibrium obtains in a solution of crystal violet we would, consequently, express as follows:⁴



Changes produced by varying the concentration of the H^+ ion produce instantaneous alteration in the ionic condition of the colored or colorless forms, as represented by the shifts in a vertical direction. In the quinoid forms, this is shown by an instantaneous change in tint. Simultaneously there begins an alteration in intensity of tint as quinoid or carbinol form shifts, ordinarily at a measurable speed, towards a condition of equilibrium. This is represented by the constitutional changes in the hori-

¹ THIS JOURNAL, 36, 99 (1914).

² Bull. soc. chim., [2] 33, 342 (1880); Compt. rend., 116, 194 (1891); Ibid., 120, 192, 264, 331, 740 (1895).

³ Ber., 12, 2348 (1879). Compare also E. Fischer and Jennings, Ber., 26, 2222 (1893).

⁴ Since a rosaniline dye is capable of adding four mols of hydrogen chloride, an additional form would seem necessary, but this would be equivalent in type to the completely ionized carbinol and may consequently be omitted.

zontal direction, which take place with the loss or addition of a molecule of water.

The present investigation was undertaken: first to ascertain the influence of changes of temperature upon the velocity of the development of color and the rate of fading of the triphenylmethane dyes; secondly, to determine to a fuller extent the effect of varying the concentration of acid and base in producing these changes; and, thirdly, to extend the work of Biddle on the neutral salt effect.

2. General Method of Procedure.

The speed of the reaction was determined in every case by following the rate of fading or of the development of color in a Stammer colorimeter. A solution of crystal violet hydrochloride was prepared in 40% alcohol containing 1 g. of dye salt per liter. Fifty cubic centimeters of this solution were diluted to one liter in 40% alcohol for a stock solution. It contained, therefore, 5×10^{-5} g. of the dye per cubic centimeter. Two cubic centimeters of the stock solution were mixed with 10 cc. of potassium hydroxide solution in each fading experiment, so that the final concentration of the dye was 8.33×10^{-6} g. per cc. The standard color for comparison was made by diluting 10 cc. of the stock solution with 50 cc. of distilled water.

In the measurements of the rate of acquiring color, a stock solution of exactly the same concentration was prepared; but before diluting to the required volume 20 cc. of normal potassium hydroxide were added to convert the dye salt into the colorless carbinol. Two cubic centimeters of this solution were mixed with 10 cc. of acid in each color development experiment. The standard for color comparison was made by adding 10 cc. of the carbinol solution to 50 cc. of acid of known concentration and the mixture was allowed to stand in a thermostat at constant temperature two hours before using.

In order to determine the velocity constant with a fair degree of precision, an air thermostat was constructed in which the colorimeter and solutions could be held at any required temperature. The thermoregulator was sufficiently sensitive to insure a temperature constant within 0.2° . The apparatus consisted of an asbestos lined box provided with glass windows through which the thermometers, regulator, fan and colorimeter scale could be observed. Two arm holes were provided to allow the operator to mix the solutions and place them in tubes in the instrument without removing them from the air bath. When not in use the arm holes were covered with felt pads.

The source of heat was a bank of electric lights connected to the light circuit through a relay which was connected in turn with a mercury-toluene thermoregulator. The air in the apparatus was kept in rapid circulation by means of an electric fan. The standard color solutions

stood in flasks on shelves in the air bath two hours before using, this time being required to insure equilibrium in the reaction. A much shorter time would suffice to bring the solutions to the constant temperature of the air bath. The reaction mixture for comparison with the standard color was prepared as follows: Two cc. of the carbinol solution (or dye) were run from a long-stemmed buret into one arm of a branched tube, Fig. 1. Ten cc. of acid (or base) were then delivered from a buret into the other branch of the tube. The tube was stoppered and placed in the thermostat, care being exercised to avoid mixing the two solutions. From six to ten of these tubes were prepared for each concentration of acid or base used at each temperature, so that the results tabulated below are average results of six or more separate determinations in each case. The exact time of mixing the solutions in the branched tubes was determined by means of a stop watch provided with a mercury contact for the second hand and connected with a battery and an electric bell. One-minute intervals were thus announced by the ringing of the bell. The branched tube was vigorously shaken without removing it from the thermostat and its contents were transferred to a 50 mm. tube and inserted in the colorimeter. Readings were taken at two-, three-, or four-minute intervals, the bell relieving the operator of the necessity of simultaneously watching the clock and matching the colors.

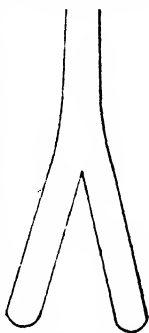


Fig. 1.

The amount of carbinol changed in a given time is proportional to the length of column of standard solution required to match the color produced, and therefore the length of column may be substituted for the concentration of the colored form. The reaction is monomolecular with respect to the dye and the velocity constants were calculated from the equations $K_1 = 1/t \log a/a - x$ and $K_2 = 1/t_2 - t_1 \log a - x_1/a - x_2$. If x is the length in mm. of the column of standard color solution required at any time to match the color produced in a 50 mm. tube, then the value $(a - x)$ is obtained by subtracting from fifty the reading in millimeters on the colorimeter scale. In the fading experiments the colorimeter reading gives directly the value of $(a - x)$ since the reading approaches zero as the reaction approaches equilibrium.

3. Temperature Coefficient (Colorless to Colored).

The following tables give the velocity constants for crystal violet at four temperatures with varying concentrations of acid. The normality of the acid given in connection with each table refers to the free hydrochloric acid present in the solution after mixing the components and deducting the amount of acid neutralized by the excess of potassium hydroxide in the carbinol solution.¹

¹ A slight excess of base is necessary to hold the dye in the colorless form but the excess is easily estimated by titration. See Biddle, *THIS JOURNAL*, 36, 84 (1914).

CRYSTAL VIOLET, TABLES I TO XIX.

TABLE I.—TEMP. 25°. 0.0026 N HCl.

| Time. Min. | Reading (X). | K ₁ . | K ₂ . |
|---------------|-----------------|------------------|------------------|
| 2 | 18.5 | 0.1010 | 0.1010 |
| 4 | 30.0 | 0.0995 | 0.0979 |
| 6 | 37.4 | 0.0998 | 0.1003 |
| 8 | 42.1 | 0.1001 | 0.1013 |
| 10 | 45.0 | 0.1000 | 0.0993 |
| Mean, | | 0.1001 | 0.1000 |

TABLE II.—TEMP. 30°. 0.0026 N HCl.

| Time. Min. | Reading (X). | K ₁ . | K ₂ . |
|---------------|-----------------|------------------|------------------|
| 2 | 27.2 | 0.1705 | 0.1705 |
| 4 | 40.0 | 0.1747 | 0.1789 |
| 6 | 44.9 | 0.1652 | 0.1462 |
| 8 | 47.6 | 0.1648 | 0.1637 |
| Mean, | | 0.1688 | 0.1648 |

TABLE III.—TEMP. 35°. 0.0026 N HCl.

| | | | |
|-------|------|--------|--------|
| 2 | 36.0 | 0.2764 | 0.2764 |
| 3 | 42.5 | 0.2746 | 0.2711 |
| 4 | 46.0 | 0.2742 | 0.2730 |
| Mean, | | 0.2751 | 0.2735 |

TABLE IV.—TEMP. 25°. 0.0051 N HCl.

| | | | |
|-------|------|--------|--------|
| 4 | 10.5 | 0.0255 | 0.0255 |
| 8 | 18.8 | 0.0256 | 0.0256 |
| 12 | 24.8 | 0.0247 | 0.0231 |
| 16 | 29.9 | 0.0247 | 0.0245 |
| 20 | 33.6 | 0.0242 | 0.0220 |
| Mean, | | 0.0249 | 0.0242 |

TABLE V.—TEMP. 30°. 0.0051 N HCl.

| | | | |
|-------|------|--------|--------|
| 6 | 22.0 | 0.0419 | 0.0419 |
| 8 | 26.9 | 0.0419 | 0.0417 |
| 10 | 31.0 | 0.0420 | 0.0424 |
| 12 | 34.3 | 0.0419 | 0.0414 |
| 14 | 36.6 | 0.0408 | 0.0344 |
| Mean, | | 0.0412 | 0.0403 |

TABLE VI.—TEMP. 35°. 0.0051 N HCl.

| | | | |
|-------|------|--------|--------|
| 4 | 25.0 | 0.0750 | 0.0750 |
| 6 | 32.2 | 0.0745 | 0.0737 |
| 8 | 36.7 | 0.0717 | 0.0632 |
| 10 | 40.2 | 0.0706 | 0.0663 |
| 12 | 43.0 | 0.0710 | 0.0730 |
| Mean, | | 0.0726 | 0.0703 |

TABLE VII.—TEMP. 40°. 0.0051 N HCl.

| | | | |
|-------|------|--------|--------|
| 4 | 34.1 | 0.1243 | 0.1243 |
| 6 | 40.5 | 0.1201 | 0.1118 |
| 8 | 44.5 | 0.1198 | 0.1186 |
| 10 | 46.8 | 0.1193 | 0.1176 |
| Mean, | | 0.1209 | 0.1181 |

TABLE VIII.—TEMP. 25°. 0.0068 N HCl.

| | | | |
|-------|------|--------|--------|
| 4 | 6.9 | 0.0161 | 0.0161 |
| 8 | 12.7 | 0.0159 | 0.0156 |
| 12 | 17.9 | 0.0160 | 0.0163 |
| 16 | 22.3 | 0.0160 | 0.0160 |
| 20 | 26.1 | 0.0160 | 0.0160 |
| Mean, | | 0.0160 | 0.0160 |

TABLE IX.—TEMP. 30°. 0.0068 N HCl.

| | | | |
|-------|------|--------|--------|
| 4 | 11.6 | 0.0286 | 0.0286 |
| 8 | 19.7 | 0.0271 | 0.0257 |
| 12 | 24.7 | 0.0246 | 0.0195 |
| 16 | 30.4 | 0.0254 | 0.0277 |
| 20 | 33.9 | 0.0246 | 0.0213 |
| Mean, | | 0.0261 | 0.0246 |

TABLE X.—TEMP. 35°. 0.0068 N HCl.

| | | | |
|-------|------|--------|--------|
| 4 | 17.1 | 0.0454 | 0.0454 |
| 8 | 27.6 | 0.0435 | 0.0417 |
| 12 | 35.2 | 0.0440 | 0.0449 |
| 16 | 40.1 | 0.0439 | 0.0436 |
| 20 | 43.2 | 0.0433 | 0.0407 |
| Mean, | | 0.0440 | 0.0439 |

TABLE XI.—TEMP. 40°. 0.0068 N HCl. TABLE XII.—TEMP. 25°. 0.0151 N HCl.

| Time Min. | Reading (X). | K ₁ . | K ₂ . | Time. Min. | Reading (X). | K ₁ . | K ₂ . |
|--------------|-----------------|------------------|------------------|---------------|-----------------|------------------|------------------|
| 4 | 24.5 | 0.0731 | 0.0731 | 4 | 4.4 | 0.0100 | 0.0100 |
| 6 | 31.7 | 0.0727 | 0.0720 | 12 | 12.0 | 0.0099 | 0.0099 |
| 8 | 37.0 | 0.0731 | 0.0742 | 20 | 18.0 | 0.0096 | 0.0093 |
| 10 | 40.7 | 0.0730 | 0.0722 | 28 | 22.9 | 0.0095 | 0.0090 |
| 12 | 43.4 | 0.0732 | 0.0744 | 36 | 27.2 | 0.0094 | 0.0093 |
| Mean, | | 0.0730 | 0.0732 | Mean, | | 0.0096 | 0.0095 |

TABLE XIII.—TEMP. 30°. 0.0151 N HCl. TABLE XIV.—TEMP. 35°. 0.0151 N HCl.

| | | | | | | | |
|-------|------|--------|--------|-------|------|--------|--------|
| 4 | 6.6 | 0.0153 | 0.0153 | 8 | 18.5 | 0.0251 | 0.0251 |
| 8 | 12.3 | 0.0153 | 0.0152 | 12 | 25.1 | 0.0252 | 0.0255 |
| 12 | 17.2 | 0.0152 | 0.0151 | 16 | 30.2 | 0.0251 | 0.0248 |
| 16 | 21.5 | 0.0152 | 0.0152 | 20 | 34.0 | 0.0246 | 0.0228 |
| 20 | 25.3 | 0.0153 | 0.0155 | 24 | 37.1 | 0.0244 | 0.0233 |
| Mean, | | 0.0153 | 0.0153 | Mean, | | 0.0255 | 0.0243 |

TABLE XV.—TEMP. 40°. 0.0151 N HCl. TABLE XVI.—TEMP. 25°. 0.0234 N HCl.

| | | | | | | | |
|-------|------|--------|--------|-------|------|--------|--------|
| 8 | 27.3 | 0.0428 | 0.0428 | 4 | 4.0 | 0.0090 | 0.0090 |
| 10 | 31.3 | 0.0426 | 0.0421 | 12 | 11.0 | 0.0089 | 0.0089 |
| 12 | 34.6 | 0.0426 | 0.0421 | 20 | 17.3 | 0.0092 | 0.0095 |
| 14 | 37.5 | 0.0429 | 0.0453 | 28 | 22.0 | 0.0089 | 0.0084 |
| 16 | 39.6 | 0.0432 | 0.0449 | 36 | 26.1 | 0.0088 | 0.0085 |
| Mean, | | 0.0430 | 0.0434 | Mean, | | 0.0090 | 0.0089 |

TABLE XVII.—TEMP. 30°. 0.0234 N HCl. TABLE XVIII.—TEMP. 35°. 0.0234 N HCl.

| | | | | | | | |
|-------|------|--------|--------|-------|------|--------|--------|
| 8 | 12.1 | 0.0150 | 0.0150 | 8 | 18.1 | 0.0243 | 0.0243 |
| 16 | 21.2 | 0.0149 | 0.0149 | 12 | 24.6 | 0.0245 | 0.0247 |
| 24 | 28.3 | 0.0150 | 0.0153 | 16 | 29.7 | 0.0246 | 0.0243 |
| 32 | 33.5 | 0.0149 | 0.0148 | 20 | 33.7 | 0.0243 | 0.0238 |
| 36 | 35.6 | 0.0149 | 0.0147 | 24 | 36.7 | 0.0239 | 0.0221 |
| Mean, | | 0.0150 | 0.0149 | Mean, | | 0.0243 | 0.0238 |

TABLE XIX.—TEMP. 40°. 0.0234 N HCl.

| Time. Min. | Reading (X). | K ₁ . | K ₂ . |
|---------------|-----------------|------------------|------------------|
| 8 | 26.1 | 0.0400 | 0.0400 |
| 10 | 30.1 | 0.0400 | 0.0397 |
| 12 | 33.5 | 0.0400 | 0.0406 |
| 14 | 36.2 | 0.0399 | 0.0388 |
| 16 | 38.5 | 0.0398 | 0.0395 |
| Mean, | | 0.0399 | Mean, 0.0397 |

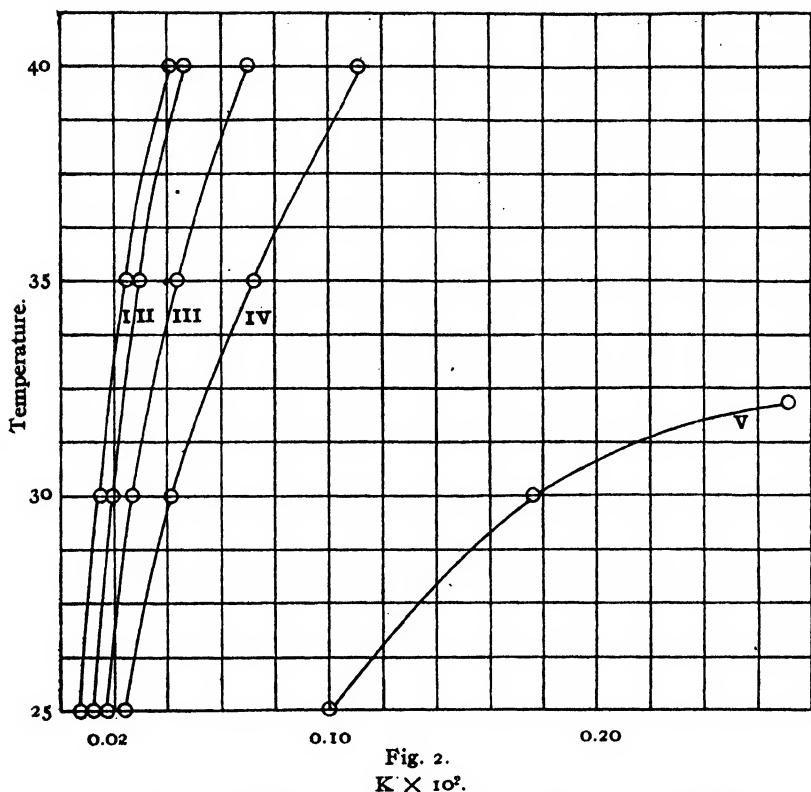


Fig. 2.
 $K \times 10^2$.

These results are plotted in Fig. 2. The velocity constants multiplied by 100 are represented as abscissae and temperature as ordinates. The curves refer to crystal violet in various concentrations of hydrochloric acid as follows:

Curve I, 0.0234 *N* HCl; II, 0.0151 *N* HCl; III, 0.0068 *N* HCl; IV, 0.0051 *N* HCl; V, 0.0026 *N* HCl.

Within the range of these experiments the temperature coefficient appears to be independent of the concentration of the acid employed. A rise of five degrees increases the velocity 66%. We may, therefore, express the relationship between the velocities at temperatures t_1 and t_2 by the empirical formula

$$K_{t_2} = K_{t_1}(1.1066)^{t_2 - t_1}$$

or employing the more general formula proposed by Arrhenius,

$$\log \frac{K_{t_2}}{K_{t_1}} = A(t_2 - t_1),$$

the value of the constant A is found to be 0.044.

This equation enables us to calculate the error in the above results, due to the heat of solution of 2 cc. of 40% alcohol in 10 cc. of dilute acid. The rise in temperature varies slightly with the concentration of the acid and temperature of the components before mixing. The maximum eleva-

tion of temperature in the above experiments reached 0.6° . The rate of cooling was such that in every instance the temperature of the mixture in the color comparison tube was within 0.4° of the temperature of the air bath at the end of four minutes. The exact temperature of the air bath was attained in from twelve to fifteen minutes.

Rejecting the readings taken during the first four minutes and applying the above formula in the calculation of the error we find that the maximum deviation of temperature introduces variation in the third decimal place of the velocity constant. It is evident then that in the experiments that were completed within fifteen minutes the constants reported have no real significance beyond the third decimal place. In very rapid reactions the readings made within the first four minutes have been retained, but the results in these cases cannot be exact.

Table XX gives the ratios between the velocity constants (K_1) at different temperatures for various concentrations of hydrochloric acid. The ratio is quite constant for any five-degree interval, being apparently independent of the temperature and also independent of the concentration of the acid.

TABLE XX.

| Concentration of acid. | $\frac{K_1^{30^\circ}}{K_1^{25^\circ}}$ | $\frac{K_1^{35^\circ}}{K_1^{30^\circ}}$ | $\frac{K_1^{40^\circ}}{K_1^{35^\circ}}$ |
|------------------------|---|---|---|
| 0.0026 <i>N</i> | 1.68 | 1.63 | * |
| 0.0051 <i>N</i> | 1.68 | 1.73 | 1.67 |
| 0.0068 <i>N</i> | 1.61 | 1.68 | 1.66 |
| 0.0151 <i>N</i> | 1.58 | 1.67 | 1.68 |
| 0.0234 <i>N</i> | 1.67 | 1.63 | 1.65 |

Average ratio, 1.66.

* With 0.0026 *N* acid at 40° the reaction ran to completion within two minutes.

4. Temperature Coefficient (Colored to Colorless).

In the fading reaction the temperature coefficient is smaller than in the reverse change. It is independent of the concentration of the base and has the same value for all temperatures between 25° and 40° as indicated in Tables XXI to XXXII.

In each case the concentration of the dye was 8.33×10^{-6} g. per cubic centimeter.

CRYSTAL VIOLET, TABLES XXI—XXXII.

TABLE XXI.—TEMP. 25° . 0.0033 *N* KOH. TABLE XXII.—TEMP. 30° . 0.0033 *N* KOH.

| Time. | Reading ($a-x$). | K_1 . | K_2 . | Time. | Reading ($a-x$). | K_1 . | K_2 . |
|-------|-----------------------|---------|---------|-------|-----------------------|---------|---------|
| 12 | 29.6 | 0.0189 | 0.0189 | 12 | 24.7 | 0.0255 | 0.0255 |
| 15 | 25.9 | 0.0190 | 0.0193 | 16 | 18.5 | 0.0263 | 0.0313 |
| 18 | 22.8 | 0.0189 | 0.0184 | 20 | 14.3 | 0.0266 | 0.0279 |
| 21 | 20.0 | 0.0189 | 0.0189 | 24 | 11.2 | 0.0266 | 0.0265 |
| 24 | 17.5 | 0.0190 | 0.0193 | 28 | 8.8 | 0.0265 | 0.0261 |
| Mean, | | 0.0189 | 0.0190 | Mean, | | 0.0263 | 0.0274 |

TABLE XXIII.—TEMP. 35°. 0.0033 *N*
KOH.

| Time. | Reading ($\alpha - \pi$). | K_1 . | K_2 . |
|-------|--------------------------------|---------|---------|
| 12 | 17.6 | 0.0378 | 0.0378 |
| 16 | 12.6 | 0.0374 | 0.0363 |
| 20 | 8.7 | 0.0379 | 0.0402 |
| 24 | 6.2 | 0.0377 | 0.0367 |
| 28 | 4.4 | 0.0377 | 0.0372 |
| Mean, | | 0.0377 | 0.0377 |

TABLE XXIV.—TEMP. 40°. 0.0033 *N*
KOH.

| Time. | Reading ($\alpha - \pi$). | K_1 . | K_2 . |
|-------|--------------------------------|---------|---------|
| 10 | 14.6 | 0.0534 | 0.0534 |
| 12 | 11.4 | 0.0534 | 0.0537 |
| 14 | 8.9 | 0.0535 | 0.0537 |
| 16 | 6.9 | 0.0537 | 0.0552 |
| 18 | 5.4 | 0.0536 | 0.0532 |
| Mean, | | 0.0535 | 0.0538 |

TABLE XXV.—TEMP. 25°. 0.0050 *N*
KOH.

| | | | |
|-------|------|--------|--------|
| 9 | 27.4 | 0.0290 | 0.0290 |
| 12 | 22.4 | 0.0290 | 0.0291 |
| 15 | 18.4 | 0.0289 | 0.0284 |
| 18 | 15.0 | 0.0290 | 0.0295 |
| 21 | 12.3 | 0.0289 | 0.0286 |
| Mean, | | 0.0290 | 0.0289 |

TABLE XXVI.—TEMP. 30°. 0.0050 *N*
KOH.

| | | | |
|-------|------|--------|--------|
| 6 | 28.8 | 0.0399 | 0.0399 |
| 9 | 22.0 | 0.0396 | 0.0389 |
| 12 | 16.6 | 0.0399 | 0.0407 |
| 15 | 12.5 | 0.0401 | 0.0410 |
| 18 | 9.5 | 0.0400 | 0.0397 |
| Mean, | | 0.0399 | 0.0400 |

TABLE XXVII.—TEMP. 35°. 0.0050 *N*
KOH.

| | | | |
|-------|------|--------|--------|
| 6 | 22.5 | 0.0578 | 0.0578 |
| 8 | 17.5 | 0.0569 | 0.0545 |
| 10 | 13.5 | 0.0568 | 0.0563 |
| 12 | 10.4 | 0.0568 | 0.0566 |
| 14 | 8.0 | 0.0568 | 0.0569 |
| Mean, | | 0.0570 | 0.0564 |

TABLE XXVIII.—TEMP. 40°. 0.0050 *N*
KOH.

| | | | |
|-------|------|--------|--------|
| 8 | 10.7 | 0.0837 | 0.0837 |
| 10 | 7.4 | 0.0829 | 0.0801 |
| 12 | 5.1 | 0.0826 | 0.0808 |
| 14 | 3.5 | 0.0825 | 0.0817 |
| 16 | 2.4 | 0.0824 | 0.0819 |
| Mean, | | 0.0828 | 0.0816 |

TABLE XXIX.—TEMP. 25°. 0.0083 *N*
KOH.

| | | | |
|-------|------|--------|--------|
| 6 | 25.7 | 0.0481 | 0.0481 |
| 9 | 18.3 | 0.0485 | 0.0468 |
| 12 | 12.9 | 0.0469 | 0.0506 |
| 15 | 8.8 | 0.0502 | 0.0553 |
| 18 | 6.3 | 0.0494 | 0.0483 |
| Mean, | | 0.0474 | 0.0498 |

TABLE XXX.—TEMP. 30°. 0.0083 *N*
KOH.

| | | | |
|-------|------|--------|--------|
| 6 | 20.0 | 0.0663 | 0.0663 |
| 9 | 12.7 | 0.0662 | 0.0660 |
| 12 | 8.2 | 0.0655 | 0.0633 |
| 15 | 5.5 | 0.0639 | 0.0578 |
| 18 | 3.5 | 0.0639 | 0.0637 |
| Mean, | | 0.0651 | 0.0634 |

TABLE XXXI.—TEMP. 35°. 0.0083 *N*
KOH.

| | | | |
|-------|------|--------|--------|
| 4 | 21.1 | 0.0936 | 0.0936 |
| 6 | 13.7 | 0.0937 | 0.0937 |
| 8 | 9.0 | 0.0930 | 0.0912 |
| 10 | 5.9 | 0.0928 | 0.0916 |
| 12 | 3.9 | 0.0923 | 0.0898 |
| Mean, | | 0.0931 | 0.0920 |

TABLE XXXII.—TEMP. 40°. 0.0083 *N*
KOH.

| | | | |
|-------|------|--------|--------|
| 4 | 14.5 | 0.1344 | 0.1344 |
| 6 | 7.8 | 0.1344 | 0.1346 |
| 8 | 4.3 | 0.1331 | 0.1293 |
| 10 | 2.4 | 0.1318 | 0.1266 |
| Mean, | | 0.1334 | 0.1312 |

The ratio between the velocity constants at four temperatures with varying concentrations of potassium hydroxide are given in Table XXXIII.

TABLE XXXIII.

| Concentration of base. | $\frac{K_1^{30^\circ}}{K_1^{25^\circ}}$ | $\frac{K_1^{35^\circ}}{K_1^{30^\circ}}$ | $\frac{K_1^{40^\circ}}{K_1^{35^\circ}}$ |
|------------------------|---|---|---|
| | | | |
| 0.0033 <i>N</i> | 1.40 | 1.44 | 1.44 |
| 0.0050 <i>N</i> | 1.38 | 1.43 | 1.48 |
| 0.0083 <i>N</i> | 1.38 | 1.42 | 1.43 |

Average ratio, 1.43.

Employing the formula $\log K_h/K_{h_1} = A(t_2 - t_1)$ we may calculate with fair precision the constant at any temperature if the constant at any other temperature is known. In this case $A = 0.03107$. Or we may employ the equation $K_h = K_{h_1}(1.074)^{t-t_1}$. The acceleration per five degrees is 43%. Since the temperature effect per degree is smaller than in the acid reactions the error due to the heat of solution of the alcohol is also smaller.

The velocity constants for the fading reactions are plotted as abscissae and the concentration of alkali as ordinates in Fig. 3.

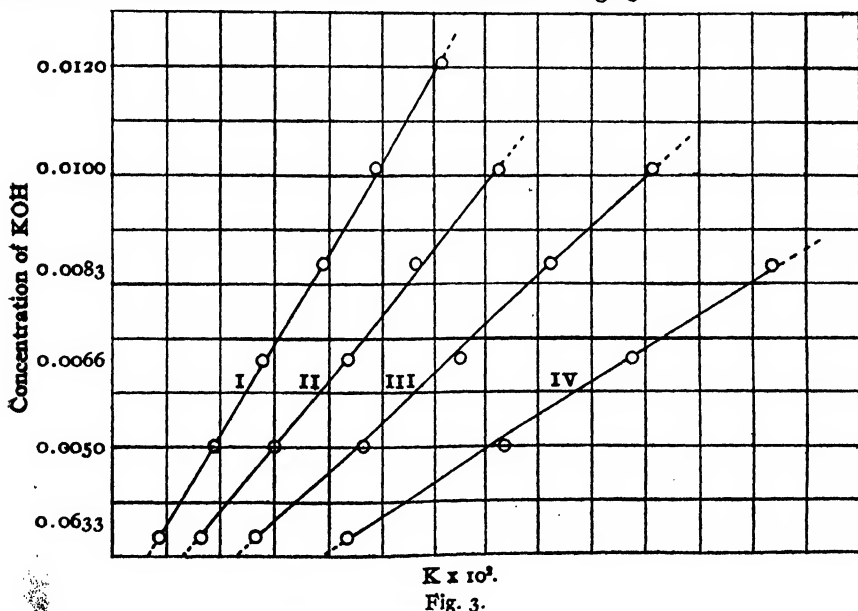


Fig. 3.

The curves are isothermals showing the relation of velocity of fading, concentration of alkali and temperature. Curve I is at 25°; II, 30°; III, 35°; and IV, 40°.

5. Effect of OH Ion upon the Speed of the Reaction.

The rate of fading of triphenylmethane dyes, under the influence of an alkali, increases with increasing concentration of the alkali. In the case

of basic dyes the rate is exactly proportional to the concentration of the hydroxyl ions. In the case of acid dyes, such as phenolphthalein, the increase in the velocity of fading is slightly in excess of the increase in the concentration of the hydroxyl ions. The results obtained with phenolphthalein are given in Table XXXIV.

TABLE XXXIV.—PHENOLPHTHALEIN IN ALKALINE SOLUTION AT 25°.

| | | | | |
|-----------------------|--------|--------|--------|--------|
| Normality of KOH..... | 0.11 | 0.15 | 0.22 | 0.33 |
| K ₁ *..... | 0.0280 | 0.0420 | 0.0707 | 0.1048 |
| K ₂ *..... | 0.0280 | 0.0418 | 0.0715 | 0.1042 |

* Average values of many determinations. Reported in this form for economy of space.

6. Effect of H⁺ Ion upon the Speed of the Reaction.

Under the direction of Professor Biddle a monamino triphenylmethane was synthesized by J. N. Lahiri¹ and the observation was made that the rate of development of color is an inverse function of the concentration of the hydrogen ions. The dye was, however, so faintly basic that the salt formed was largely hydrolyzed and the intensity of the color was insufficient for accurate measurement. The speeds of the corresponding reactions with diamino derivatives were determined by Sidgwick and Moore² and Sidgwick and Rivett³ who found the velocity of color development to be proportional to the two-thirds power of the acid concentration. With a triamino derivative Biddle⁴ found that, within a certain range, the speed of acquiring color is inversely proportional to the square of the hydrogen ion concentration.

Extending these researches over a wider range of acid concentration, the interesting fact is disclosed that each of these basic triphenylmethane derivatives acquires color at a rate varying with the concentration of the acid in such a way that the rate passes through a minimum at a certain definite acid concentration. The possibility of this effect was pointed out by Adams and Rosenstein in the case of crystal violet.⁵ The particular concentration corresponding to the minimum is different for the different dyes. That is to say, increasing the acid content of the reaction mixture, up to a certain limit, retards the speed of the reaction, but increasing the quantity of acid beyond that limit accelerates the change.

Thus for crystal violet the constants at 25° are as follows:

| | | | | | | |
|------------------------|---------|---------|---------|---------|---------|---------|
| Normality of acid..... | 0.0432 | 0.0234 | 0.0151 | 0.0068 | 0.0051 | 0.0026 |
| K ₁ | 0.01170 | 0.00899 | 0.00969 | 0.01628 | 0.02482 | 0.10009 |

This is shown graphically in Fig. 4.

¹ Unpublished Thesis, 1914, U. of Cal.

² *J. Chem. Soc.*, 95, 889 (1909).

³ *Ibid.*, 95, 899 (1909).

⁴ *THIS JOURNAL*, 36, 84 (1914).

⁵ *Ibid.*, 36, 1452 (1914).

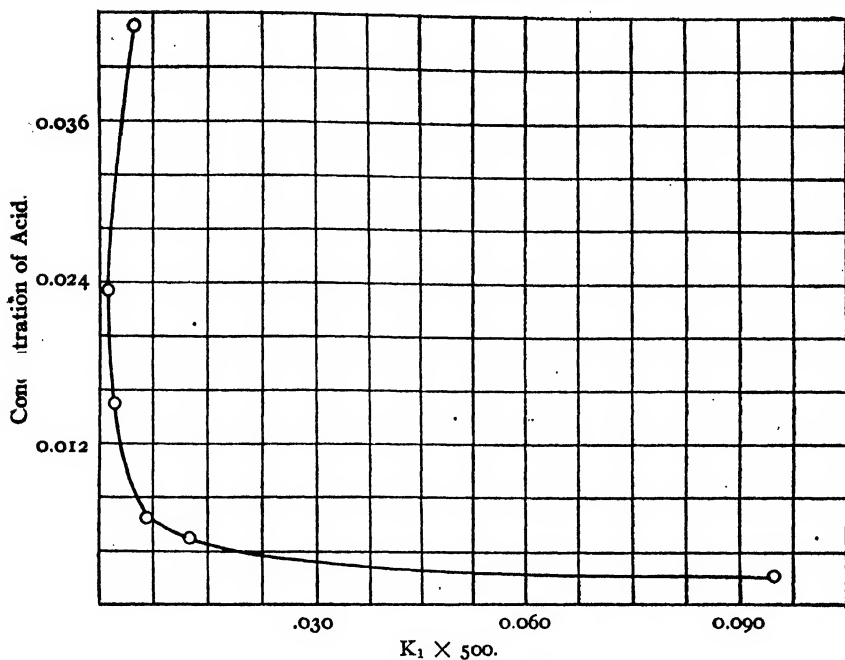


Fig. 4.

The minimum rate corresponds to a concentration of approximately 0.0234 *N* hydrochloric acid. In the case of malachite green the acid concentration corresponding to the minimum rate is approximately 0.007 *N*. This is indicated in Table XXXV.

It must be remembered, however, that these velocity constants are measures of the rates of approach to the colors of equilibrium mixtures in each of the given acid concentrations and not measures of the absolute velocities of reaction. The values are, therefore, not strictly comparable.¹ Table XXXV shows the effect of varying the acid concentration on malachite green carbinol.

TABLE XXXV.—MALACHITE GREEN. TEMPERATURE 25°.

| | | | | | | |
|-----------------------|--------|--------|--------|--------|--------|--------|
| Normality of HCl..... | 0.065 | 0.023 | 0.015 | 0.007 | 0.005 | 0.003 |
| K_1 | 0.1224 | 0.1092 | 0.0645 | 0.0480 | 0.0559 | 0.0628 |
| K_2 | 0.1227 | 0.1101 | 0.0672 | 0.0465 | 0.0553 | 0.0623 |

7. The Neutral Salt Effect.

In many types of chemical change in which acids or bases are active catalysts the velocity constants are changed by the addition of small quantities of neutral salts. This phenomenon was investigated by Arrhenius² in connection with the rate of hydrolysis of cane sugar. He found

¹ See Biddle, *THIS JOURNAL*, 36, 90 (1914).

² *Z. physik. Chem.*, 31, 197 (1899).

that the speed of the reaction was increased to practically the same extent by equimolecular quantities of neutral salts if these salts were equally ionized. Salts having the smallest dissociation constants were least effective. He observed, moreover, that any particular salt produces a greater relative change in the presence of dilute acid than in more concentrated acid solutions. And Arrhenius attributed the salt effect to more than one cause, *e. g.*, the direct catalyzing influence of the salt molecules, and the formation of new electrolytes in the solution. Euler¹ made a similar explanation and suggested that the ionization of the solvent may be increased by the presence of salts and the catalytic influence of the salt is largely due to this effect. Acree,² on the other hand, believes "that catalysis by salts or other neutral substances is due not so much to a change in the dissociation constant of the water as to a number of other factors" which he enumerates as effects of the salt upon the viscosity of the solution, the solvation of the ions and undissociated molecules, the combination of the salt with the molecules undergoing transformation, and the influence of the salt upon the thermodynamic potentials of the reacting ions or molecules.

Stieglitz³ has expressed the opinion that the salt effect "is due to the fact that in salt solutions we are working with mixed solvents in which ionization, velocities, etc., cannot be expected to be the same as in a pure solvent."

In the results tabulated below are set forth the neutral salt effects upon reaction velocities which occur in transformations of dyes of the triphenylmethane series. Measurements have been made of the rates of change from the quinoid to the benzoid forms, and also the reverse changes, in the case of crystal violet and malachite green in the presence of varying quantities of neutral uniunivalent salts. Qualitative observations have been made of the effects of unibivalent and bibivalent salts under like conditions. Similar measurements have been carried out on the influence of neutral salts upon the fading of phenolphthalein in the presence of alkalis. The fading of the latter indicator, with and without neutral salts, has been a subject of study by Drs. E. Q. Adams and Merl Randall⁴ and the effect of neutral salts upon the ionization of the indicator was investigated by Rosenstein.⁵ Tables XXXVI to XLIX inc. refer to crystal violet.

Table XI, shows the effect of sodium chloride. Each constant reported is the average of at least twenty readings. (Five readings at regular time intervals on each of at least four reaction mixtures.)

¹ *Z. physik. Chem.*, 32, 348 (1900).

² *Am. Chem. J.*, 41, 475 (1909).

³ *THIS JOURNAL*, 34, 1687 (1912).

⁴ Unpublished investigation.

⁵ *THIS JOURNAL*, 36, 93 (1914).

TABLE XXXVI.—0.004 *N* HCl,
0.004 *N* KCl.

| Time. | Reading (α). | K ₁ . | K ₂ . |
|-------|-----------------------|------------------|------------------|
| 12 | 30.2 | 0.0337 | 0.0337 |
| 14 | 33.2 | 0.0338 | 0.0356 |
| 16 | 35.5 | 0.0336 | 0.0319 |
| 18 | 37.6 | 0.0336 | 0.0339 |
| 20 | 39.5 | 0.0338 | 0.0361 |
| Mean, | | 0.0337 | 0.0342 |

TABLE XXXVII.—0.004 *N* HCl,
0.092 *N* KCl.

| Time. | Reading (α). | K ₁ . | K ₂ . |
|-------|-----------------------|------------------|------------------|
| 12 | 18.0 | 0.0161 | 0.0161 |
| 15 | 21.6 | 0.0163 | 0.0172 |
| 18 | 24.6 | 0.0163 | 0.0161 |
| 21 | 27.5 | 0.0165 | 0.0175 |
| 24 | 29.9 | 0.0164 | 0.0163 |
| Mean, | | 0.0163 | 0.0166 |

TABLE XXXVIII.—0.004 *N* HCl,
0.183 *N* KCl.

| Time | Reading | K ₁ | K ₂ |
|-------|---------|----------------|----------------|
| 12 | 15.2 | 0.0131 | 0.0131 |
| 15 | 18.0 | 0.0121 | 0.0121 |
| 18 | 20.7 | 0.0128 | 0.0126 |
| 21 | 22.8 | 0.0124 | 0.0108 |
| 24 | 25.0 | 0.0125 | 0.0122 |
| Mean, | | 0.0125 | 0.0121 |

TABLE XXXIX.—0.004 *N* HCl,
0.362 *N* KCl.

| Time | Reading | K ₁ | K ₂ |
|-------|---------|----------------|----------------|
| 9 | 9.6 | 0.0103 | 0.0103 |
| 12 | 12.6 | 0.0105 | 0.0111 |
| 15 | 15.3 | 0.0105 | 0.0108 |
| 18 | 18.0 | 0.0107 | 0.0117 |
| 21 | 20.0 | 0.0105 | 0.0093 |
| Mean, | | 0.0105 | 0.0106 |

TABLE XL.—CRYSTAL VIOLET IN 0.004 *N* HCl WITH NaCl.

| | | | | |
|------------------------|--------|--------|--------|--------|
| Normality of NaCl..... | 0.004 | 0.092 | 0.183 | 0.362 |
| K ₁ | 0.0334 | 0.0186 | 0.0133 | 0.0105 |
| K ₂ | 0.0333 | 0.0188 | 0.0133 | 0.0102 |

It is evident that the rate of developing color in crystal violet becomes slower as the concentration of the salt increases and a comparison of Table XL with the results given in Tables XXXVI to XXXIX reveals the fact that equimolecular quantities of KCl and NaCl are equally effective in retarding the change. The rate of development of color is likewise retarded by the presence of salts as indicated in Tables XLI to XLIX.

CRYSTAL VIOLET IN ALKALINE SOLUTIONS.

TABLE XLI.—0.0104 *N* KOH. No SALT.

| Time. | Reading ($\alpha - x$). | K ₁ . | K ₂ . |
|-------|---------------------------|------------------|------------------|
| 10 | 13.0 | 0.0585 | 0.0585 |
| 12 | 9.9 | 0.0577 | 0.0591 |
| 14 | 7.6 | 0.0577 | 0.0574 |
| 16 | 5.8 | 0.0578 | 0.0586 |
| 18 | 4.4 | 0.0580 | 0.0599 |
| Mean, | | 0.0579 | 0.0587 |

TABLE XLII.—0.0104 *N* KOH, 0.284 *N* NaCl.

| Time. | Reading ($\alpha - x$). | K ₁ . | K ₂ . |
|-------|---------------------------|------------------|------------------|
| 10 | 16.9 | 0.0471 | 0.0471 |
| 12 | 13.7 | 0.0468 | 0.0465 |
| 14 | 11.0 | 0.0468 | 0.0471 |
| 16 | 8.8 | 0.0470 | 0.0484 |
| 18 | 7.1 | 0.0470 | 0.0466 |
| Mean, | | 0.0469 | 0.0471 |

TABLE XLIII.—0.0104 *N* KOH,
0.608 *N* NaCl.

| Time. | Reading ($\alpha - x$). | K ₁ . | K ₂ . |
|-------|------------------------------|------------------|------------------|
| 10 | 20.0 | 0.0397 | 0.0398 |
| 12 | 16.6 | 0.0399 | 0.0404 |
| 14 | 13.5 | 0.0406 | 0.0448 |
| 16 | 11.5 | 0.0399 | 0.0348 |
| 18 | 9.5 | 0.0400 | 0.0414 |

Mean, 0.0400 0.0402

TABLE XLIV.—0.0104 *N* KOH,
1.045 *N* NaCl.

| Time. | Reading ($\alpha - x$). | K ₁ . | K ₂ . |
|-------|------------------------------|------------------|------------------|
| 6 | 31.6 | 0.0332 | 0.0332 |
| 8 | 27.2 | 0.0330 | 0.0325 |
| 10 | 23.4 | 0.0339 | 0.0326 |
| 12 | 20.0 | 0.0331 | 0.0327 |
| 16 | 14.7 | 0.0330 | 0.0327 |

Mean, 0.0332 0.0327

TABLE XLV.—0.0104 *N* KOH,
1.562 *N* NaCl.

| | | | |
|----|------|--------|--------|
| 10 | 26.9 | 0.0269 | 0.0269 |
| 12 | 24.3 | 0.0261 | 0.0220 |
| 14 | 21.8 | 0.0257 | 0.0235 |
| 16 | 18.5 | 0.0270 | 0.0256 |
| 18 | 16.3 | 0.0270 | 0.0274 |

Mean, 0.0265 0.0262

TABLE XLVI.—0.0104 *N* KOH,
2.139 *N* NaCl.

| | | | |
|----|------|--------|--------|
| 10 | 30.1 | 0.0220 | 0.0220 |
| 12 | 27.0 | 0.0223 | 0.0236 |
| 14 | 24.0 | 0.0227 | 0.0266 |
| 16 | 22.0 | 0.0222 | 0.0188 |
| 18 | 20.0 | 0.0221 | 0.0206 |

Mean, 0.0226 0.0228

The following condensed tables show similar results with different salts acting in conjunction with potassium hydroxide at various concentrations:

TABLE XLVII.—CRYSTAL VIOLET IN 0.013 *N* KOH WITH KNO₃.

| Normality of KNO ₃ | 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|-------------------------------------|--------|--------|--------|--------|--------|--------|
| K ₁ | 0.0712 | 0.0520 | 0.0411 | 0.0350 | 0.0309 | 0.0259 |
| K ₂ | 0.0715 | 0.0524 | 0.0413 | 0.0356 | 0.0305 | 0.0259 |

TABLE XLVIII.—CRYSTAL VIOLET IN 0.013 *N* KOH WITH KCl.

| Normality of KCl..... | 0.0 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 |
|-----------------------|--------|--------|--------|--------|--------|--------|
| K ₁ | 0.0712 | 0.0540 | 0.0440 | 0.0380 | 0.0328 | 0.0290 |
| K ₂ | 0.0715 | 0.0545 | 0.0440 | 0.0381 | 0.0328 | 0.0290 |

TABLE XLIX.—CRYSTAL VIOLET IN 0.062 *N* KOH WITH NaCl.

| Normality of NaCl..... | 0.000 | 0.116 | 0.194 | 0.388 | 0.775 | 0.966 |
|------------------------|--------|--------|--------|--------|--------|--------|
| K ₁ | 0.3592 | 0.2812 | 0.2212 | 0.1840 | 0.1442 | 0.1373 |
| K ₂ | 0.3610 | 0.2796 | 0.2191 | 0.1796 | 0.1469 | 0.1408 |

The rate of fading is approximately a linear function of the square root of the equivalent concentration of the salt as shown in Fig. 5.

The following tables, L and LI, show the salt effect on the rate of fading of phenolphthalein in different concentrations of alkali and salt. It will be observed that the salt effect is exactly opposite to that produced by salts in crystal violet. In other words, the rate of fading of phenolphthalein is accelerated by salts:

TABLE L.—PHENOLPHTHALEIN IN 0.31 *N* KOH WITH NaCl.

| Normality of NaCl..... | 0.000 | 0.116 | 0.194 | 0.388 | 0.966 | 1.940 |
|------------------------|--------|--------|--------|--------|--------|--------|
| K ₁ | 0.1048 | 0.1204 | 0.1360 | 0.1451 | 0.1553 | 0.1625 |
| K ₂ | 0.1041 | 0.1213 | 0.1357 | 0.1439 | 0.1518 | 0.1627 |

TABLE LI.—PHENOLPHTHALEIN IN 0.11 *N* KOH WITH NaCl.

| | | | |
|------------------------|--------|--------|--------|
| Normality of NaCl..... | 0.14 | 0.28 | 0.42 |
| K_1 | 0.0323 | 0.0358 | 0.0419 |
| K_2 | 0.0315 | 0.0361 | 0.0419 |

In this study, as indicated by the tables, we find that neutral salts in the presence of basic dyes behave like acids. That is to say, the addition of a quantity of a neutral salt to a solution of an acid dye, such as phenolphthalein, when fading under the influence of an alkali, produces

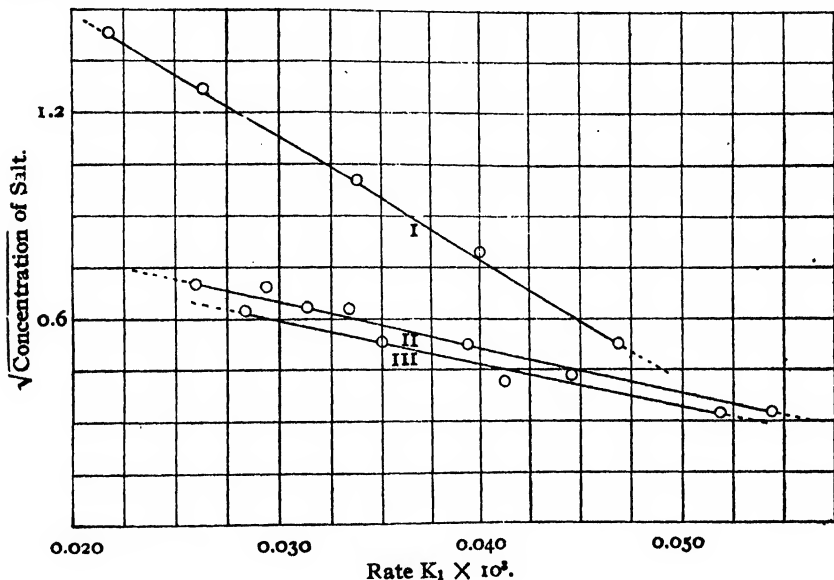


Fig. 5.

Square roots of salt concentrations are plotted as ordinates and rates of fading as abscissae. Curve I summarizes Tables XLII to XLVI (inc.); Curves II and III represent the values reported in Tables XLVIII and XLVII, respectively.

an acceleration equivalent to that effected by increasing the concentration of the alkali; while a similar addition of salt to a basic dye such as crystal violet or malachite green when shifting under the influence of either acid or base towards a state of equilibrium produces an effect equivalent to that resulting from the addition of an acid. This means that the speed of fading of a basic dye in the presence of an alkali will in all cases be diminished by the addition of a neutral salt. In the conversion of such a dye from the carbinol to the colored form in the presence of an acid, the salt effect will be determined by the concentration of the acid and may be accelerating, retarding, or indifferent. It will be recalled that for each carbinol base there is a particular concentration of acid at which the color is developed at a minimum rate. In acids of this particular concentration, neutral salts are without effect. In solutions of higher acid con-

centration, they are found to accelerate the development of color, and in less concentrated solutions with respect to the acid, they retard the rate of assumption of color.

Misses Alice Morse and Lulu E. Vance¹ found the catalyzing effect of such uniuivalent neutral salts as sodium chloride, potassium chloride, sodium nitrate, sodium bromide, sodium iodide and potassium nitrate, to be the same in equimolecular quantities within the limits of experimental error. The results recorded in Tables XLVIII to LVIII confirm this conclusion in the case of the salts studied. Unibivalent salts of bibivalent salts, however, give variable results. This, as previously shown,² is to be accounted for in these cases by the variation of hydrogen ion produced by partial hydrolysis. From an inspection of Tables XXXIV to XLI it will be noted, further, that the salt effect is greatest in solutions most dilute with respect to the acid. The effect, as will be seen, decreases with increasing concentration of the acid until the acid concentration producing the minimum rate is reached. Thereafter, the effect of the salt, though slight, increases with increasing concentration. In the fading experiments it will also be noted that the salt effect is greatest in solutions of greatest dilution with respect to the alkali.

Not only is the rate of change altered by neutral salts, the equilibrium is itself displaced, as was previously pointed out by Biddle.³ This is evident from the fact that in acid solutions, the colors produced vary with the amount of salt added, the direction of the variation being the same as that produced by increasing concentration of acid.

There is apparently no simple mathematical relation between the quantity of salt employed and the changes in velocity for the conversion of benzoid to quinoid form in the presence of acids. In the conversion of colored to colorless form, in the presence of alkalies, however, a fairly regular decrease in rate is produced by increasing concentration of salt. The rate of fading is almost a linear function of the square root of the equivalent concentration of the salt (Fig. 5). In the presence of a concentration of base exceeding 0.02 *N*, however, there is considerable deviation from this rule. In such cases the graph obtained by plotting the speed against the square root of the sum of the concentrations of salt and alkali, more closely approximates a straight line.

Alcohol and acetone accelerate the rate of fading of crystal violet, brilliant green and other basic derivatives of triphenylmethane. They also accelerate the development of color. The effect is therefore just opposite to that produced by salts. The change in rate is relatively

¹ Unpublished Thesis carried out under the direction of H. C. Biddle, Univ. of California, 1914.

² Biddle, *THIS JOURNAL*, 36, 98 (1914).

³ *Ibid.*, 36, 86, 96 (1914).

greater as the concentration of the alcohol or acetone increases, in this respect also differing from the behavior of neutral salts. The addition of sugar reduces the rate of fading, but this is probably due to a diminution of the hydroxyl ions caused by combination of the base with the sugar molecules to form glucosates. It is possible practically to stop the progress of the fading reaction by the addition of sufficient sugar.

Summary.

1. The temperature coefficient for the conversion of a triphenylmethane carbinol into the quinoid form, in the presence of an acid, is independent of the concentration of the acid and between 25° and 40° independent also of the temperature. For crystal violet the increase in the velocity of the change is 66% for every five degrees. Changes of the same order of magnitude were observed in the case of diamino derivatives but comparatively few measurements were made with these dyes and the results have not been tabulated in this paper.

2. The temperature coefficient for the fading of a triphenylmethane dye in the presence of an alkali is independent of the concentration of the base and independent of the temperature (between $25-40^{\circ}$). For crystal violet the increase in velocity is 43% for five degrees.

3. For all concentrations of acid below 0.024 *N* the speed of the color development in crystal violet is an inverse function of the concentration of the hydrogen ions. For all concentrations of acid above this value the velocity is a direct function of the hydrogen ion concentration.

4. The rate of fading of a triphenylmethane dye is a direct function of the concentration of the hydroxyl ions and in the case of basic dyes, such as crystal violet, is exactly proportional to such concentration.

5. Neutral salts retard the rate of fading and also retard the rate of development of color in all the basic triphenylmethane dyes but accelerate the rate of fading of acidic dyes.

6. All uniunivalent neutral salts in equivalent concentrations are equally effective in modifying the catalytic influence of the acid or base. They behave like acids in their effect upon basic dyes and like bases in their influence upon acid dyes.

BERKELEY, CAL.

CONVERSION OF GALACTOSE PENTACETATE TO AN ISOMERIC FORM.

BY C. S. HUDSON AND H. O. PARKER.¹

Received April 10, 1915.

Crystalline galactose pentacetate was prepared by Erwig and Koenigs²

¹ Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture, and the Chemical Laboratory of Princeton University.

² *Ber.*, 22, 2207 (1889).

by the acetylation of galactose with acetic anhydride and sodium acetate. They found that the substance melts at 142° , and their analysis shows that its percentages of carbon, hydrogen and acetyl agree closely with the theoretical values for a galactose pentacetate. Fischer and Armstrong¹ found the specific rotation of the substance to be $+7.48^{\circ}$ in benzene solution. We have prepared a considerable quantity of this pentacetate by the indicated method, using the proportions 4 parts of sugar, one of anhydrous sodium acetate and 16 of acetic anhydride, have purified it without difficulty by recrystallization from alcohol, and have confirmed the quoted data on the melting point and the specific rotation in benzene. In chloroform solution (*chloroformum purificatum*, U. S. P.) we find dextro-rotation of the value $(\alpha) = +25^{\circ}$.

Erwig and Koenigs² mention that the boiling of this pentacetate with acetic anhydride and a little zinc chloride yields a sirupy product. We have investigated this change and find that there is produced a second galactose pentacetate which may be readily crystallized.

Fifty grams of the first pentacetate (m. p. 142°) were heated on the steam bath with 150 cc. of acetic anhydride containing 10 g. zinc chloride until the specific rotation changed from $+28^{\circ}$ to the constant value of $+105^{\circ}$, the reaction being complete within about fifteen minutes. The mixture was then poured into 500 cc. ice water, neutralized with sodium bicarbonate, and the solution extracted with chloroform, in which the acetates of the sugars are very soluble. The greater part of the chloroform was removed by distilling under reduced pressure, followed by evaporation in a strong air current. The residue was mixed with 95% alcohol to form a thick sirup and it was not difficult to bring about crystallization by scratching the wall of the glass container. The crystals were purified by several recrystallizations from alcohol until the specific rotation became constant.

The yield was about 70% of the weight of the first acetate. The substance, which we would designate for the present the second pentacetate of galactose,³ melts sharply at 95.5° .

On combustion, 0.2631 and 0.2746 g. subs. yielded 0.4727 and 0.4945 g. CO_2 and 0.1325 and 0.1385 g. H_2O .

Found: C = 48.99 and 49.10%; H = 5.52 and 5.60%. Theoretical, 49.23 and 5.64 for a hexose pentacetate.

The saponification of several half-gram samples of the substance by boiling 3 hours with 0.25 N sulfuric acid gave values ranging between 54.3 and 54.9% CH_3CO . Theory, 55.1. The saponification of the substance with alcoholic potash yielded crystalline galactose, which was identified by its specific rotation.

The specific rotations of the new pentacetate (m. p. 95.5°) in several solvents, all the rotations being in the right-hand direction, are recorded in the table.

¹ Ber., 35, 838 (1902).

² Loc. cit.

³ In the following article a third crystalline pentacetate of galactose is described, and on account of its existence it appears preferable to avoid the designations α , β and γ until the relationship of these acetates to the α - and β -forms of galactose is established.—C. S. H.

| Solvent. | Chloroform. | | | Benzene. | | Methyl alcohol. | Glacial acetic acid. |
|-------------------------------------|-------------|---------|---------|----------|--------|-----------------|----------------------|
| Grams pentacetate per 100 cc. soln. | 3.2500 | 3.3376 | 4.0084 | 1.6816 | 2.2412 | 3.9480 | 3.3732 |
| $[\alpha]_D^{20}$ | +106.7° | +106.9° | +106.1° | +94.8° | +92.3° | +113.6° | +114.0° |

The second galactose pentacetate was crystallized also from the products of the acetylation of galactose with acetic anhydride and zinc chloride but the yield was so small that this method is not recommended.

Our thanks are expressed to Mr. A. S. Eastman, who has kindly verified some of the work.

WASHINGTON, D. C.

THE EXISTENCE OF A THIRD CRYSTALLINE PENTACETATE OF GALACTOSE.

By C. S. HUDSON.¹

Received April 10, 1915.

The acetylation of an aldose sugar with acetic anhydride and sodium acetate (the Liebermann method) has yielded the fully acetylated β -derivative in all cases in which a crystalline product was obtained. If one acetylates either the α - or β -form of glucose by this reaction, substantially the same product is obtained, namely, β -glucose pentacetate, mixed with a small proportion of sirupy acetylation products. It would seem probable in these cases that at least a small proportion of the isomeric alpha acetate is produced along with the larger amount of the beta derivative, and some months ago the writer undertook a careful search for the presence of the second pentacetate of galactose as a side product in the preparation of the first pentacetate² of this sugar by the Liebermann reaction. The acetates of galactose were chosen for the experiments because of the fact that the one which must be removed from the mixed products in order to permit the possible crystallization of the second pentacetate is a decidedly crystalline substance of low solubilities. On this plan, 400 g. of very pure galactose, prepared in the laboratory from lactose, were acetylated in the manner indicated and poured into cold water. About 275 g. of the first pentacetate of galactose (m. p. 142°) were obtained after one recrystallization from 95% alcohol of the crude crystalline product which did not dissolve in the water. The water was extracted with chloroform and this solution was mixed with the mother liquor from the crystallization of the first pentacetate and the chloroform allowed to evaporate slowly at room temperature. The sirupy residue crystallized somewhat in the course of several days, and these crystals proved to be more of the first pentacetate. The mother liquor from them later crystallized

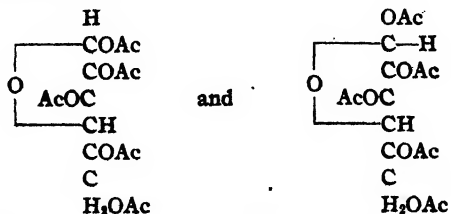
¹ Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture.

² See the preceding article in regard to the existence of these first and second pentacetates.

further, and after recrystallization from alcohol about 15 g. of a substance was obtained which melted at 96° . It was supposed that this was the product sought, namely, the second galactose pentacetate, which had been found to melt at $95-6^{\circ}$.¹ Later, an occasion arose to examine the specific rotation of this substance, which had not been done before because it was believed that its melting point characterized it sufficiently, and to my surprise it showed levorotation, $[\alpha]_D^{20} = -41^{\circ}$ in chloroform solution. The first pentacetate of galactose, melting at 142° , has $[\alpha]_D^{20} = +25$, the second, melting at $95-6^{\circ}$ shows $[\alpha]_D^{20} = +107$, both being of dextrorotation. The levorotatory substance must therefore be considered a new acetate of galactose. At this stage Dr. J. M. Johnson undertook the further examination of these three acetates of galactose, an investigation which is now in progress, and I am much indebted to him for the following data which show that the new acetate is in reality a third pentacetate of galactose. From 175 g. of galactose he obtained by the method which has been described above, except with the improvement of neutralizing the aqueous solution with sodium bicarbonate before extracting it with chloroform, 163 g. of the first pentacetate of galactose (m. p. 142°), and sufficient of the new levorotatory acetate to yield 20 g. of it after several recrystallizations from alcohol to bring it to a constant rotation. This pure material showed $[\alpha]_D^{20} = -41.6^{\circ}$ in chloroform and melted at 98° . This temperature is thus quite distinct from that at which the second pentacetate melts, $95-96^{\circ}$, though of course the specific rotation of the latter, $+107^{\circ}$, fully distinguishes it from the new acetate. Saponification of the levorotatory acetate with alcoholic potash yielded crystalline galactose, which was recrystallized and identified by its initial and final specific rotations.

Acetyl determinations made by boiling half-gram samples with 100 cc. of 0.25 *N* H_2SO_4 during three hours, indicated 54.6 and 54.8% acetyl (CH_3CO). Theoretical value for a galactose pentacetate, 55.1. The value for a tetracetate is only 49.4%. Mol. wt. determinations in benzene solution by the freezing-point method gave values between 386 and 404. Theoretical for a galactose pentacetate, 390.

These data show that the substance is a third crystalline pentacetate of galactose. From a theoretical standpoint the existence of three such isomers is noteworthy because, while two of them may be assigned the usual stereomeric structures,



¹ See the preceding article by Hudson and Parker.

the existence of a third isomer must be accounted for on other grounds. It is possible of course that the third form may have the oxygen ring linkage on some other than the gamma carbon atom. This is the suggestion which Fischer¹ has recently made in connection with his discovery of a third modification of methyl glucoside which he obtained in the form of a distillable sirup. As mentioned, Dr. Johnson and myself are continuing the investigation of the isomerism of the three galactose pentacetates.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE NORTHWESTERN UNIVERSITY MEDICAL SCHOOL.]

ON THE COMBINATION OF PROTEIN WITH HALOGEN ACIDS.²

BY J. H. LONG AND MARY HULL.

Received April 28, 1915.

Certain classes of combinations between protein bodies and halogen acids, and, in particular, hydrochloric acid, have been studied and frequently described. Before the full recognition of the fact that the proteins may act as basic bodies and hold these acids in salt forms, the distinction between such salts and substitution compounds was not clearly made. Hydriodic acid, for example, forms salts with egg albumin, but it forms also substitution products in which the iodine replaces hydrogen in nucleus groups. In this manner relatively large amounts of iodine may be added, but the products lose the properties of proteins.

In the production of these compounds and in the determination of the proportions in which proteins and halogen acids unite, a number of quite different processes have been employed. The results vary with the process and we are still without a satisfactory answer to some phases of the general question. Among the earliest papers describing definite combinations between proteins and acid those of Paal³ may be referred to. Paal produced compounds which he considered as definite salts of peptones, containing from 10 to 15% of HCl. These were made by treatment of egg albumin with diluted acid and also by digestion of the protein by acid and pepsin. In these cases the salts were separated in comparatively pure form, but in most inquiries on the subject the aim has been to determine the ratio of combination between protein and halogen, rather than the isolation of the actual compounds. This has been done, usually, by finding the amount of acid held by a given weight of protein, when an excess is added and this excess measured by the aid of an appropriate indicator. In this manner, for example, Osborne⁴ showed, by use

¹ *Ber.*, 47, 1980 (1914).

² Presented at the New Orleans meeting of the American Chemical Society, April 2, 1915.

³ C. Paal, *Ber.*, 25, 1202 (1892); 27, 1827 (1894).

⁴ *THIS JOURNAL*, 21, 477 and 486 (1899).

of tropaeolin, that 1 g. of certain proteins will bind from 9 to 13 cc. of 0.1 N HCl. With the pure protein edestin, the mean amount was 12.7 cc. or 46.3 mg. This is 4.63% of the protein weight. Panormow¹ described definite molecular combinations of albumins with several acids which were obtained by mixing the proteins with dilute acids and precipitating by alcohol. The weights of hydrochloric and other acids combined in this manner appear from the analyses, however, to be rather low. In one case a hydrochloride contained HCl amounting to about 3.2% of the weight of the protein.

By aid of titrations with Guenzburg's reagent, Hoffa found that serum albumin will combine with about 6.3% of its weight of HCl, while the albumoses from egg albumin will combine with about 7.7%. These values become greatly increased as the proteins undergo digestion.²

Spiro and Pemsel³ followed a different method to determine the amount of acid which may be combined by proteins. This was based on the fact that the hydrochlorides or other combinations may be salted out as are the proteins themselves. By adding an excess of 0.2 N or 0.1 N acid to the protein solution, then a sufficient amount of ammonium sulfate solution for precipitation, the uncombined excess of acid may be titrated in the filtrate. Results are given for egg and serum albumins. For the former the amount of HCl combined was about 5% of the protein weight, and for the latter about 7% in the mean.

By following the general method of Cohnheim and Krieger, results were found by Erb⁴ which show a far greater maximum combining power of HCl than is indicated by the work of other observers. These results cannot be reconciled with the values obtained by Spiro and Pemsel, who did not observe any marked increase in the amount of HCl held when the weight mixed with the protein is increased. In the Erb experiments the amount of HCl held by 1 g. of serum albumin increases from 104 mg. to 204 mg. when the volume of 0.1 N acid used in solution is quadrupled. However, by use of a method identical in principle v. Rhorer⁵ reached the conclusion that the acid held by the protein does not vary as claimed by Erb. He showed, further, that the method followed by Erb could not be expected to yield accurate results. This conclusion seems justified by the facts.

We have sought to throw some light on the problem by working in a

¹ *J. russ. phys.-chem. Gesell.*, 31, 556 (1899) and 32, 249 (1900); through *Jahresb. Fortschr. Thier-Chemie*, 29, 8 (1899) and 30, 6 (1900).

² *Jahresb. Fortschr. Thier-Chemie*, 30, 52 (1900).

³ *Z. physiol. Chem.*, 26, 233 (1898).

⁴ *Chem. Centr.*, 1901, II, 359. Cohnheim, "Chemie der Eiweisskoerper," 126.

⁵ *Arch. ges. Physiol.*, 90, 368 (1902). See also the discussion by Robertson, in *Ergebnisse der Physiologie*, 10, 216 (1910), where there is a very full citation of the literature.

very simple manner and by methods which at first sight might not be expected to give definite results. Our investigations grew out of some experiments intended to show the extent of combination between the acids and solid or coagulated proteins, and the behavior of these compounds on hydrolysis.¹ In our experiments we have added known volumes of diluted acids to known weights of proteins and have dried the mixtures at a low temperature or over sulfuric acid, followed by drying over solid alkali. It will be seen that reasonably constant results may be secured in this way which have some meaning.

While the titration of the excess of free acid standing over a mixture of acid and protein cannot give a correct measure of the acid which may be held, because of the ready dissociation of such compounds with liberation of acid, and because, also, of the behavior of available indicators in presence of unaltered protein, still the results in this way have some value for comparison. Some of the results reported by other workers, and referred to above, were thus secured, for example, those by Osborne cited.

We made mixtures of coagulated egg albumin with 25 cc. of 0.1 *N* HCl and 25 cc. of water and treated them as described below. The albumin used was in the form of dried, soluble, egg albumin which was weighed out in multiples of gram portions, dissolved and poured into a large excess of boiling distilled water containing a little dilute acetic acid. By pouring slowly and stirring constantly it is possible in this way to secure a very fine uniform coagulum. For each gram of weighed egg powder the protein in the coagulum amounts to 700 mg. Methyl orange was finally added to the mixed protein and acid, and the free acid determined. The difference between this and the acid added is calculated as acid held. The results are of course below the truth, somewhat. Some of these residual titrations were made at once and some after certain intervals. In some cases the acid solution and protein were mixed by stirring, without further agitation. In other experiments the mixtures were actively shaken in flasks and then allowed to stand, while, finally, in other experiments, the protein and acid were well rubbed together in a mortar. Table I gives the results secured.

The table discloses the fact that, even after long standing, the combination between acid and protein is incomplete if the mixture is simply stirred. Even after thorough shaking the same is true, but constant results come speedily when the mixture are well rubbed in the mortar. We secure practically the same end result from the solid protein, in this manner, that others have reported for protein solutions. The egg albumin combines with about 3% of its weight of HCl, when heat is not applied, and this represents a somewhat constant value for the combination as

¹ See paper in a recent number of *THIS JOURNAL*, by one of us, "On the Physiological Behavior of Combined Hydrochloric Acid," 37, 1333.

measured by indicators. For other proteins the results are not necessarily the same, of course.

TABLE I.

| | Coag. from gm. egg. | Wt. of HCl held. | | | |
|---------------------------------------|---------------------------|------------------|------------------|------------------|------------------|
| | | At once. | After 30 min. | After 60 min. | After 90 min. |
| Mixture made without shaking..... | 1 | 0.0065 | 0.0112 | 0.0183 | 0.0189 |
| | 2 | 0.0102 | 0.0205 | 0.0284 | 0.0339 |
| | 3 | 0.0204 | 0.0412 | 0.0500 | 0.0525 |
| Mixture made by active shaking..... | 1 | 0.0076 | 0.0175 | 0.0200 | 0.0211 |
| | 2 | 0.0193 | 0.0295 | 0.0394 | 0.0423 |
| | 3 | 0.0306 | 0.0554 | 0.0605 | 0.0660 |
| Mixture made by rubbing in mortar.... | 1 | 0.0206 | 0.0222 | 0.0215 | 0.0219 |
| | 2 | 0.0425 | 0.0429 | 0.0419 | 0.0430 |
| | 3 | 0.0690 | 0.0700 | 0.0773 | 0.0740 |

By heating the proteins with dilute acid solutions on the water bath and evaporating slowly to dryness an increase in weight follows which corresponds to the addition of the acid and not to addition of acid plus water, which would be the case if hydrolysis had taken place. This is illustrated by the following experiments in which a constant weight of fibrin was mixed with increasing volumes of 0.2 *N* HCl, evaporated slowly to dryness, and weighed after heating to practically constant weight in the electric oven to 105°. The dry weight of the fibrin alone was 0.677 g. After weighing, the residue was mixed with carbonate and nitrate and fused. In the melt the HCl was determined by the Volhard method.

TABLE II.

| No. | Cc. 0.2 <i>N</i> HCl. | Mg. HCl. | Dry wt. | Inc. wt. | HCl found. |
|--------|-----------------------|----------|---------|----------|------------|
| 1..... | 20.0 | 146.0 | 0.740 | 0.063 | 0.0635 |
| 2..... | 15.0 | 109.5 | 0.743 | 0.066 | 0.0642 |
| 3..... | 12.5 | 91.2 | 0.745 | 0.068 | 0.0640 |
| 4..... | 10.0 | 73.0 | 0.742 | 0.065 | 0.0666 |
| 5..... | 7.5 | 54.8 | 0.730 | 0.053 | 0.0519 |
| 6..... | 5.0 | 36.5 | 0.704 | 0.027 | 0.0330 |
| 7..... | 2.5 | 18.3 | 0.696 | 0.019 | 0.0176 |

The determination of the chlorine is much more accurate than is that of the dry weight. It is somewhat difficult to bring the protein, with or without the acid, to a constant weight, but the results show a satisfactory degree of constancy. In Nos. 1, 2, 3 and 4 it is evident we have added a great excess of acid, and that the excess was expelled without adding water by hydrolysis. An amount of acid below that in No. 5 is insufficient to saturate the protein, under these conditions. The mean increase in weight for the first four mixtures is 0.0655, while the mean HCl addition in the same 0.0646. It is evident that we have no water addition here. In similar experiments made with egg albumin the mean increase in weight was 0.0680 and the mean HCl content 0.0704.

With this point established the greater number of experiments were concerned with the extent of the halogen acid addition, rather than with the gross weight increase. The experiments were made essentially in the same manner, using casein, fibrin and egg albumin.

Casein and HCl.

TABLE III.

In each test 750 mg. anhydrous casein employed. Evaporated over live steam.

| No. | Cc. 0.2 N HCl. | Mg. HCl. | Mg. HCl held. | Mean of first four. |
|--------|----------------|----------|---------------|---------------------|
| 1..... | 20.0 | 146.0 | 69.5 | 70.9 |
| 2..... | 15.0 | 109.5 | 72.4 | |
| 3..... | 12.5 | 91.2 | 70.3 | |
| 4..... | 10.0 | 73.0 | 71.4 | |
| 5..... | 7.5 | 54.8 | 52.0 | |
| 6..... | 5.0 | 36.5 | 34.9 | |
| 7..... | 2.5 | 18.3 | 17.2 | |

TABLE IV.

750 mg. of anhydrous casein plus HCl.

| No. | Cc. 0.2 N HCl. | Mg. HCl. | Mg. HCl held. | Mean of first four. |
|--------|----------------|----------|---------------|---------------------|
| 1..... | 20.0 | 146.0 | 66.6 | 67.8 |
| 2..... | 15.0 | 109.5 | 68.8 | |
| 3..... | 12.5 | 91.2 | 67.5 | |
| 4..... | 10.0 | 73.0 | 68.5 | |
| 5..... | 7.5 | 54.8 | 45.8 | |
| 6..... | 5.0 | 36.5 | 32.9 | |
| 7..... | 2.5 | 18.3 | 16.4 | |

As several experiments suggested that a high temperature might have the effect of causing the addition of too much acid, accompanied by some hydrolysis, the later tests were made by evaporating on a water bath, and slowly. Table IV shows the results secured by this condition of evaporation.

With the lower temperature the acid held is somewhat less and amounts to 9.04% of the weight of the casein. It is clear that no excess of acid is added in the cases where an excess of acid was mixed with the casein at the outset. The capacity for combination seems to be a constant in this respect, but apparently varies with the temperature. This result, which is confirmed by many others, seems to disprove completely the view of Erb, referred to above, that the amount of acid taken up by the protein increases with the amount added.

Fibrin and HCl.

The fibrin used for these tests was thoroughly washed until white, mixed with toluene and pressed out as dry as possible, after passing a number of times through the meat chopper. The mass so prepared holds enough toluene to keep some weeks unchanged, at a low temperature. It is not necessary to freeze it. The experiments were made as with the casein, by evaporating slowly on a water bath. Two independent sets of experiments, A and B, are given in Table V.

The results here for the larger acid concentrations are very regular and close to a mean value. They are somewhat higher than the corresponding results for the casein and show, as we found there, that no increase in the amount of HCl combined follows from increase in amount added to the fibrin.

TABLE V.
2.5 g. fibrin = 750 mg. protein, plus HCl.

| No. | Cc. 0.2 N HCl. | Mg. HCl. | A. Mg. HCl held. | B. Mg. HCl held. | Mean of first four. |
|--------|-------------------|----------|---------------------|---------------------|------------------------|
| 1..... | 20.0 | 146.0 | 71.1 | 70.1 | 70.8 |
| 2..... | 15.0 | 109.5 | 70.0 | 70.3 | |
| 3..... | 12.5 | 91.2 | 71.1 | 72.1 | |
| 4..... | 10.0 | 73.0 | 71.1 | 70.3 | |
| 5..... | 7.5 | 54.8 | 50.7 | 51.5 | |
| 6..... | 5.0 | 36.5 | 31.9 | 32.8 | |
| 7..... | 2.5 | 18.3 | 16.4 | 17.3 | |

Egg Albumin and HCl.

We have made at different times a large number of tests as to the rate of combination between the acid and this common protein. The egg used for the purpose was referred to above, when another experiment was described. It was part of a large lot of clear dried egg white of Chinese origin which was selected because of its solubility and low color, and which we have used as a standard preparation for a number of years. In these experiments a known amount was weighed and coagulated, as explained above, and small portions of the coagulum, to correspond to 750 mg. of anhydrous protein, taken for each test. Volumes of 0.2 N HCl were added as in the other tests and the mixtures evaporated slowly to dryness on the water bath. After this the residue was dried at 105° to a constant weight. As the coagulum holds a large amount of water the dry weights taken are not as accurately defined as with the casein or the fibrin.

Two sets of experiments are here given, A and B, Table VI.

TABLE VI.
1.07 g. egg = 750 mg. protein, plus HCl.

| No. | Cc. 0.2 N HCl. | Mg. HCl. | A. Mg. HCl held. | B. Mg. HCl held. | Mean of first four. |
|--------|-------------------|----------|---------------------|---------------------|------------------------|
| 1..... | 20.0 | 146.0 | 80.3 | 70.3 | 77.7 |
| 2..... | 15.0 | 109.5 | 84.0 | 80.3 | |
| 3..... | 12.5 | 91.2 | 81.8 | 83.6 | |
| 4..... | 10.0 | 73.0 | 70.3 | 71.2 | |
| 5..... | 7.5 | 54.8 | 51.5 | 52.9 | |
| 6..... | 5.0 | 36.5 | 32.8 | 35.0 | |
| 7..... | 2.5 | 18.3 | 17.3 | 16.0 | |

The values for the egg combination are not as uniform as were the others, but it is clear that no excess of HCl is held by the higher concentrations. Egg albumin seems to have a higher binding power than has fibrin or casein, the relations, calculated for the gram basis, being:

Casein, 90.4, or 9.04%; fibrin, 94.4, or 9.44%; egg albumin, 103.6, or 10.36%.

These values are much higher than are those found by means of indicators, and undoubtedly have as definite a meaning. Before going into any further discussion concerning them, the results given in corresponding experiments with hydrobromic acid and hydriodic acid will be given.

Hydrobromic Acid and Protein.

Portions of the three proteins were treated with 0.2 *N* HBr exactly in the manner given for HCl. The bromine was found after fusion of the dry residue.

TABLE VII.

750 mg. of anhydrous casein plus HBr.

| No. | Cc. 0.2 <i>N</i> HBr. | Mg. HBr. | Mg. HBr held. | Mean of first four. |
|---------|-----------------------------|-------------|---------------------|---------------------------|
| 1..... | 30.0 | 485.7 | 273.0 | 273.9 |
| 2..... | 27.5 | 445.2 | 274.0 | |
| 3..... | 25.0 | 404.8 | 275.0 | |
| 4..... | 20.0 | 323.8 | 273.5 | |
| 5..... | 15.0 | 242.8 | 227.4 | |
| 6..... | 12.5 | 202.4 | 193.8 | |
| 7..... | 10.0 | 161.9 | 153.4 | |
| 8..... | 7.5 | 121.4 | 116.8 | |
| 9..... | 5.0 | 80.9 | 79.1 | |
| 10..... | 2.5 | 40.5 | 39.7 | |

TABLE VIII.

2.5 g. fibrin = 750 mg. protein plus HBr.

| No. | Cc. 0.2 <i>N</i> HBr. | Mg. HBr. | Mg. HBr held. | Mean of first four. |
|---------|-----------------------------|-------------|---------------------|---------------------------|
| 1..... | 30.0 | 485.7 | 295.0 | 291.8 |
| 2..... | 27.5 | 445.2 | 286.0 | |
| 3..... | 25.0 | 404.8 | 297.0 | |
| 4..... | 20.0 | 323.8 | 289.3 | |
| 5..... | 15.0 | 242.8 | 226.8 | |
| 6..... | 12.5 | 202.4 | 190.3 | |
| 7..... | 10.0 | 161.9 | 150.9 | |
| 8..... | 7.5 | 121.4 | 114.7 | |
| 9..... | 5.0 | 80.9 | 78.7 | |
| 10..... | 2.5 | 40.5 | 40.4 | |

TABLE IX.

1.07 g. egg albumin powder = 750 mg. protein plus HBr.

| No. | Cc. 0.2 <i>N</i> HBr. | Mg. HBr. | Mg. HBr held. | Mean of first three. |
|---------|-----------------------|----------|---------------|-------------------------|
| 1..... | 30.0 | 485.7 | 376.5 | 375.3 |
| 2..... | 27.5 | 445.2 | 378.7 | |
| 3..... | 25.0 | 404.8 | 370.7 | |
| 4..... | 20.0 | 323.8 | 309.2 | |
| 5..... | 15.0 | 242.8 | 224.7 | |
| 6..... | 12.5 | 202.4 | 179.7 | |
| 7..... | 10.0 | 161.9 | 147.8 | |
| 8..... | 7.5 | 121.4 | 109.2 | |
| 9..... | 5.0 | 80.9 | 76.5 | |
| 10..... | 2.5 | 40.5 | 39.6 | |

The above results show that hydrobromic acid is taken up in large quantity by the three proteins and in amounts relatively much greater than is hydrochloric acid. For 1 g. of the proteins the acid combination is as follows:

Casein, 365 mg. or 36.5%; fibrin, 398 mg. or 38.9%; egg albumin, 500 mg. or 50%.

It is evident that the combination cannot be on the same basis as that of the hydrochloric acid, as the amounts combined are not in the proportion of 36.5 to 80.9. But the weights combined with 1 g. of protein stand in the same order for the two acids, as seen by these figures, the amount held by the casein being called 100.

HCl: Casein, 100
HBr: 100

Fibrin, 104.4
106.6

Egg albumin, 114.6
137.0

For the casein the HCl and HBr combined are in the proportion of 90.4 mg. to 365 mg. for the gram of protein, or nearly in the ratio of 5 to 9 molecules. For the HBr combination with fibrin the ratio is a little higher with reference to the HCl. For the egg albumin the HCl and HBr combinations stand to each approximately in the proportion of 5 to 11 molecules. These numbers probably have some significance, which will be taken up below.

Hydriodic Acid and Protein.

By the same general plan combinations between the three protein bodies and hydriodic acid were made. But a little study showed that the constancy in combining ratios found with the other acids is lacking here. When this acid is added to prepared proteins and the mixture evaporated the increase in weight is roughly in agreement with the iodine taken up, calculated as HI. But sometimes there is a discrepancy, and the total increase in weight may even be less than the added iodine. This can be the case only when something else is driven out of the protein molecule, that is, when a substitution, as well as an addition follows. This is seen from Tables X and XI. In the experiments made with egg and fibrin these results were secured.

TABLE X.

1.07 g. egg albumin powder equivalent to 750 mg. protein and 806 mg. dry residue plus HI.

| No. | Cc. 0.2 N HI. | Mg. HI. | Dry residue. | Inc. weight. | Mg. HI held. |
|--------|---------------|---------|--------------|--------------|--------------|
| 1..... | 30.0 | 768 | 1400 | 594 | 588 |
| 2..... | 25.0 | 640 | 1278 | 472 | 463 |
| 3..... | 20.0 | 512 | 1185 | 379 | 381 |
| 4..... | 15.0 | 384 | 1111 | 305 | 287 |
| 5..... | 12.5 | 320 | 1082 | 276 | 245 |
| 6..... | 10.0 | 256 | 1014 | 208 | 197 |
| 7..... | 7.5 | 192 | 985 | 179 | 161 |
| 8..... | 5.0 | 128 | 919 | 113 | 108 |
| 9..... | 2.5 | 64 | 866 | 60 | 53 |

In four additional experiments with the largest amount of 0.5 N acid added, 30 cc., the weight increase and HI fixed were as follows:

| | | | | | |
|-------------------------|-----|-----|-----|-----|-----------|
| Increase in weight..... | 603 | 588 | 581 | 572 | Mean, 586 |
| HI held..... | 589 | 561 | 568 | 583 | Mean, 575 |

It is somewhat difficult to dry these mixtures to constant weight, and this may account for part of the irregularity. In the course of the evaporation and final drying they become dark, which suggests the liberation of iodine, but treatment with carbon disulfide or chloroform fails to bring anything into solution. The following results were secured by repeated experiments with smaller weights of iodine added to the constant weight of egg:

TABLE XI.

1.07 g. egg powder = 750 mg. protein plus HI.

| Cc. 0.2 N HI. | Mg. HI. | Inc. wt. | Mg. HI held. |
|---------------|---------|----------|--------------|
| 25 | 640 | 436 | 410 |
| 25 | 640 | 442 | 478 |
| | | — | — |
| | | 439 | 444 |
| 20 | 512 | 415 | 379 |
| 20 | 512 | 380 | 400 |
| 20 | 512 | 390 | 394 |
| | | — | — |
| | | 395 | 391 |
| 15 | 384 | 310 | 295 |
| 15 | 384 | 299 | 298 |
| | | — | — |
| | | 305 | 397 |

In the first of the above tests in which the 30 cc. of 0.2 N HI was added, the amount held by the protein is over 76% of the weight of the protein. This cannot be accurately titrated by normal alkali, as is the case with the hydrochloric acid combinations of the egg albumin and other proteins. In these combinations the titration results and the chlorine determinations with silver nitrate, after fusion, agree. It appears, therefore, that the HI combinations by heat are of an order different from those of the HCl compounds. But the combinations made without heat are apparently similar, as will be shown below.

TABLE XII.

2.5 g. fibrin = 750 mg. dry protein plus HI.

| No. | Cc. 0.2 N HI. | Mg. HI. | Mg. HI held. |
|--------|---------------|---------|--------------|
| 1..... | 30.0 | 768 | 595 |
| 2..... | 25.0 | 640 | 409 |
| 3..... | 20.0 | 512 | 392 |
| 4..... | 15.0 | 384 | 303 |
| 5..... | 12.5 | 320 | 253 |
| 6..... | 10.0 | 256 | 210 |
| 7..... | 7.5 | 192 | 153 |
| 8..... | 5.0 | 128 | 102 |
| 9..... | 2.5 | 64 | 59 |

It has been shown in a previous paper by one of us¹ that HI combines with casein under the same conditions and to yield compounds containing for 1 g. of anhydrous casein about 575 mg. of iodine, calculated as HI. This appeared to represent the maximum combining power. Like the other combinations, these possessed an ochre color, suggesting a product resembling the iodalbose of Weyl.² This product was prepared by add-

¹ THIS JOURNAL, 29, 1334 (1907).² Z. physiol. Chem., 68, 236 (1910).

ing egg albumin to concentrated hydriodic acid at water bath heat, and pouring the mixture into an excess of water. The other precipitate which formed was purified by solution in alkali and reprecipitation. The iodine is firmly fixed in the product, which seemed to be lacking in some of the characteristic protein reactions. In all our experiments the iodine was used only in the form of dilute HI solution and in absence of heat no other-red color was developed. The concentration of the dilute acid in evaporation possibly leads to the same or similar compounds.

Some later experiments on the combination between casein and hydriodic acid, carried out as were those for the other proteins, gave the following results. The amount of iodine held is much larger than in the earlier experiments, but whether by addition or substitution is not clear. The iodine is calculated as HI.

TABLE XIII.

750 mg. dry casein plus HI.

| No. | Cc. 0.02 N HI. | Mg. HI. | Inc. in weight. | Mg. HI held. |
|--------|----------------|---------|-----------------|--------------|
| 1..... | 30.0 | 768 | 601 | 587 |
| 2..... | 25.0 | 640 | 400 | 394 |
| 3..... | 20.0 | 512 | 393 | 379 |
| 4..... | 15.0 | 384 | 329 | 306 |
| 5..... | 12.5 | 320 | 299 | 242 |
| 6..... | 10.0 | 256 | 229 | 202 |
| 7..... | 7.5 | 192 | 141 | 137 |
| 8..... | 5.0 | 128 | 112 | 100 |

Most of the compounds of iodine and protein described in the literature are substitution products, and are obtained by the action of the halogen, as solid, tincture or in KI solution. The products contain from about 5 to 15% iodine, but show reactions deviating from those of proteins in some respects. Such compounds have been described by Hofmeister,¹ Blum,² Liebrecht,³ Hopkins and Pinkus,⁴ Kurajeff,⁵ Pauly and Gundermann⁶ and others and are not to be confounded with the salts secured by treatment with weak HI. Because of the easy decomposition of the latter, however, and its marked reducing properties, iodine is liberated to be carried into the molecule.

With the hope of throwing further light on the nature of the reaction, we have repeated a number of the above experiments in such a manner as to remove the excess of acids at a low temperature. This was accomplished by adding the 0.2 N acid to the solid protein as before, and allowing the mixtures to stand some weeks over sulfuric acid to remove

¹ *Z. physiol. Chem.*, 24, 159 (1898).

² *Ibid.*, 28, 288 (1899).

³ *Ber.*, 30, 1824 (1897).

⁴ *Ibid.*, 31, 1312 (1898).

⁵ *Z. physiol. Chem.*, 26, 462 (1898).

⁶ *Ber.*, 41, 3999 (1908) and 43, 2243 (1910).

most of the water. The small evaporating dishes holding the residues were then placed in bell jars over powdered sodium hydroxide to absorb acid vapors. In this manner practically all of the acid was removed, and most of the water. The mixtures with HCl and HBr evaporated down without much color, but the HI mixtures became reddish brown, as before. A short, final drying in the air oven was necessary to bring to constant weight. Table XIV shows the final weights and the halogen content of the products.

Only the larger volumes of acid were added in these experiments.

TABLE XIV.—COMBINATION OF PROTEIN WITH HCl, HBr AND HI, AND EVAPORATION AT LOW TEMPERATURE. THE EQUIVALENT OF 750 MG. OF ANHYDROUS PROTEIN USED IN EACH CASE.

| No. | Cc. 0.2 N HCl. | Mg. HCl. | Inc. in wt. | Mg. HCl held. | Cc. 0.2 N HBr. | Mg. HBr. | Inc. in wt. | Mg. HBr held. | Cc. 0.2 N HI. | Mg. HI. | Inc. in wt. | Mg. HI held. |
|------------------|----------------------|-------------|-------------------|---------------------|----------------------|-------------|-------------------|---------------------|---------------------|------------|-------------------|--------------------|
| 1. Casein..... | 30 | 219.0 | 73 | 71 | 30 | 485.7 | 265 | 270 | 30 | 768 | 429 | 426 |
| 2. Casein..... | 25 | 182.5 | 81 | 72 | 25 | 404.8 | 274 | 268 | 25 | 640 | 400 | 415 |
| 3. Casein..... | 20 | 146.0 | 74 | 70 | 20 | 323.8 | 294 | 271 | 20 | 512 | 468 | 420 |
| 4. Casein..... | 15 | 109.5 | 73 | 73 | | | | | 15 | 384 | 382 | 371 |
| | | Mean, | | 71.5 | | Mean, | | 269.6 | | Mean, | | 420 |
| 5. Fibrin..... | 25 | 182.5 | 71 | 63 | 25 | 404.8 | 289 | 280 | 30 | 768 | 450 | 430 |
| 6. Fibrin..... | 20 | 146.0 | 65 | 62 | 20 | 323.8 | 272 | 280 | 25 | 640 | 402 | 311 |
| 7. Fibrin..... | 15 | 109.5 | 69 | 63 | 15 | 242.8 | 272 | 274 | 20 | 512 | 405 | 404 |
| | | Mean, | | 62.6 | | Mean, | | 278 | | Mean, | | 415 |
| 8. Egg alb..... | 25 | 182.5 | 77 | 71 | 25 | 404.8 | 310 | 348 | 30 | 768 | 437 | 433 |
| 9. Egg alb..... | 20 | 146.0 | 77 | 73 | 20 | 323.8 | 292 | 319 | 25 | 640 | 487 | 416 |
| 10. Egg alb..... | 15 | 109.5 | 65 | 70 | 15 | 242.8 | 224 | 232 | 20 | 512 | 413 | 390 |
| | | Mean, | | 71.3 | | Mean, | | 329 | | Mean, | | 413 |

These results are extremely interesting, as they show the extent of combination without the aid of heat. The final temperature of drying to constant weight in the electric oven was not over 75°, and this heat was not applied until all acid vapors had been absorbed in the desiccators. It will be seen that the results are very close to those secured by evaporating the acid and protein mixtures in the water bath and drying at 105°.

It is evident, therefore, that the proteins and acids unite in this manner in proportions which are apparently definite, but not in proportion to the molecular weights of the acids. The power of combination is possibly connected with the volatility of the acid, since we find that HI unites with the proteins in proportion greater than does HBr, and this, in turn, greater than HCl. Nothing is shown in the HI column of the last table which would suggest that the halogen acid addition is accompanied by the loss of water. That is, no hydrolysis appears to have taken place,

but the reaction follows as would that between glutaminic acid and hydrochloric acid, for example. In the complex protein molecules there are many of these amino groups available and the number of acid molecules which may be united to them apparently depends on the "strength" of the acid, as measured by its lower volatility.

Table XIV discloses the important fact that we have a constant combination for the hydriodic acid, when amounts above 15 cc. of the 0.2 *N* solution are used with 750 mg. of protein. For 1 g. of each protein about 553 mg. of HI goes into combination, and this evidently represents a maximum under the conditions. When heat is applied much more may be held in some form.

These halogen acid combinations, whether made by simple action of the acid on the solid protein or by this treatment followed by evaporation, undergo a rather marked degree of dissociation by contact with water. The dry hydrochloride of egg albumin gives up its acid and on this account the compound has been used to some extent as an aid to digestion. The rate of dissociation is, however, slow. Some information on this point is given in a recent publication from this laboratory in which the hydrogen concentration of HCl separated from egg albumin was measured by the gas chain method.¹ In the treatment of a given weight of a protein hydrochloride with successive equal volumes of water the acid strength of the dissociated portion gradually diminishes.

It has been shown above that the behavior of hydriodic acid with protein when evaporated is different from the behavior of the corresponding chlorine and bromine acids. But the combination as measured by indicator titration is of the same order, as shown by these results. Portions of the three substances corresponding to 750 mg. of dry protein were rubbed up in a mortar with 10 cc. of 0.2 *N* acid and washed into flasks with 10 cc. more. At the end of an hour the excess of "free" acid was found by 0.1 *N* alkali and methyl orange.

TABLE XV.—COMBINATION OF HCl, HBr AND HI WITH 750 MG. OF PROTEINS AS DESCRIBED.

| | Cc. 0.2 <i>N</i> HCl. | Cc. 0.2 <i>N</i> HBr. | Cc. 0.2 <i>N</i> HI. |
|-------------|--------------------------|--------------------------|-------------------------|
| Egg..... | 3.4 | 3.0 | 3.8 |
| Fibrin..... | 3.5 | 3.7 | 4.5 |
| Casein..... | 2.2 | 2.1 | 1.5 |

In each case the fibrin seems to hold more acid and the casein less than the egg. We should expect the same volume of acid to be combined with the different proteins. The discrepancy is probably due to the lack in delicacy in the behavior of this indicator in presence of undigested protein, but the results are close enough to show that the combinations are of the same type.

¹ THIS JOURNAL, 37, 1333 (1915).

In place of titrating directly, similar mixtures were filtered and the residues on the filter washed with successive equal portions of water, 20 cc. in each case. These washings were titrated separately. It was found that the fibrin held the acids more tenaciously than the other proteins. In seven or eight washings about one-fifth of the hydrochloric acid could be removed from the egg, a tenth from the fibrin, and a fourth, or less, from the casein. The dissociation of the hydrobromic acid is of the same order.

The behavior of hydriodic acid is most interesting here in view of the large weight held after evaporation experiments. The figures of Table XVI show the amount of 0.2 *N* NaOH required to titrate the first filtrate and successive washings in experiments with egg and fibrin.

TABLE XVI.

| | Egg. | | Fibrin. | |
|-------------------------------|-----------|-------|---------|-------|
| | a. | b. | a. | b. |
| 1st filtrate and washing..... | 13.75 cc. | 14.30 | 12.55 | 13.20 |
| 2nd filtrate and washing..... | 1.90 | 2.25 | 1.35 | 1.90 |
| 3rd filtrate and washing..... | 1.25 | 1.30 | 1.50 | 1.20 |
| 4th filtrate and washing..... | 0.90 | 0.60 | 0.70 | 0.90 |
| 5th filtrate and washing..... | 0.60 | 0.20 | 0.60 | 0.40 |
| 6th filtrate and washing..... | 0.30 | 0.00 | 0.50 | 0.20 |
| 7th filtrate and washing..... | .. | .. | 0.40 | 0.10 |
| 8th filtrate and washing..... | .. | .. | 0.20 | .. |
| 9th filtrate and washing..... | .. | .. | 0.10 | .. |
| Total..... | 18.70 | 18.65 | 18.10 | 17.90 |
| Cc. 0.2 <i>N</i> HI held..... | 1.30 | 1.35 | 1.90 | 2.10 |

It is seen that after the prolonged washings about two-thirds of the HI held by the egg is washed out and over half of that held by the fibrin, as measured by the direct titrations. While the procedure is lacking in quantitative accuracy it gives a good comparative result. It is evident that when heat is not applied the hydriodic acid is very loosely held. The type of salt produced in this way suffers extended dissociation by water.

Resume.

The experiments detailed above show that the amounts of the halogen acids which combine with casein, fibrin and egg albumin, as measured by the usual indicator titration, are low and not accurately proportional to the molecular weights of the acids. The discrepancies are probably due to the lack of delicacy of the indicator in presence of unchanged protein, on the one hand, and to the more or less complete dissociation of the protein-acid compound on the other. The latter is doubtless the more important factor, since it has been shown that a large fraction of the acid may be washed away from the protein.

When the proteins named are treated with the halogen acids of 0.2 *N* concentration, in excess, and the mixtures evaporated at a low temperature by standing over sulfuric acid some weeks, followed by similar treatment over solid alkali, and final drying to constant weight at 75°, very constant weights of acid are taken up and held by the protein. These weights of acid are not increased by the excess added, which points to the definite character of the reaction. The amounts are not proportional to the molecular weights of the acids, the combining proportion being relatively greater for HI than for HBr and greater for the latter than for HCl. But the compounds all appear to be salts of the protein molecule and contain many times as much acid as is suggested by the titration combinations. These dry salts undergo dissociation readily when mixed with water.

If the acid-protein mixtures are evaporated on the water bath, in place of being dried at a low temperature, the behavior of HCl and HBr remains essentially the same. No greater amounts of the acid are taken up by a gram of protein and we doubtless reach here a maximum in the combining power of the acid and protein. A salt of a type different from that formed in solution at a low temperature is secured. In the case of the HI, however, there is no such limit to the iodine held, and it is probable that we have here a substitution of the element in the nucleus of the protein molecule, as well as an addition of the acid. As much as 75% of the weight of the original protein may be so held and the combination has a brownish ochre color, with loss of protein reactions.

CHICAGO, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY.]

STUDIES ON THE CULTURE MEDIA EMPLOYED FOR THE BACTERIOLOGICAL EXAMINATION OF WATER.

1. THE SCHARDINGER-DUNHAM MEDIUM FOR TESTING FOR THE PRESENCE OF HYDROGEN SULFIDE FORMING BACTERIA.¹

By E. M. CHAMOT AND H. W. REDFIELD.

Received March 27, 1913.

Introduction.

Although an enormous amount of time and labor has been spent upon investigations of bacterial culture media with a view of shortening the time required for diagnostic results and producing media yielding more uniform and more constant results, a critical review of the literature fails to show, save in a few instances, that the media which have eventually been proposed have received truly systematic study and that the concentrations suggested are necessarily those which are best fitted for the purposes for which the media have been made.

¹ Papers read at the Rochester Meeting, American Chemical Society, September, 1913.

That slight variations in concentration in most of the media employed in the bacteriological examination of water may lead to relatively great differences in both quantitative and qualitative results has long been recognized and has been the basis of suggested so-called standard media, but the fact has apparently been ignored that in the selection of concentrations, those should be chosen, a slight variation from which will lead to the least possible variation in the diagnostic characters sought; will furnish dependable results in the shortest possible time; and yet will give practically identical results in the hands of different analysts and investigators.

Comparison of the data obtained by different water analysts shows such variations between wide limits, even making due allowances for the personal equation, that it is evident that our standard media need more study and possibly revision.

In the laboratories of the senior author considerable routine work is carried on in the periodic examination of waters and the control of purification plants. In this work he found that the media prepared at different times by himself and coworkers frequently failed to yield identical results.

Although it seemed probable that the only satisfactory solution of these problems lay in abandoning such variable materials as meat broth and peptone and adopting nutritive substances of definite composition—in other words, so-called “synthetic media”—an attempt was made to study the causes of the variation in results obtained in our work and thus to eventually find, if possible, a really satisfactory “synthetic” medium. With these ends in view, investigations of all the different culture media employed in water examinations were begun several years ago and will be continued until all the media have been studied.

The results obtained proved to be so interesting, curious, and at variance with what we expected that it seems worth while to present the facts in a series of articles, of which this is the first.

Part I. Historical.

In 1877 Gayon¹ published what appears to be the first recorded proof of the formation of hydrogen sulfide by bacteria acting upon albuminous material. Two years later, 1879, Miquel² succeeded in isolating from sewage, from contaminated waters and also from waters believed to be potable, an organism having the power of changing free and combined sulfur to hydrogen sulfide. Three years later Boehm³ obtained similar results with an organism isolated from well water. These results paved the way for a large amount of work upon the formation of hydrogen

¹ Gayon, *Compt. rend.*, 85, 1074 (1877).

² Miquel, *Bull. soc. chim.*, [2] 32, 127 (1879); *Ann. de l'Obser. Mont-Souris*, 1880.

³ Boehm, *Monats.*, 3, 224 (1882).

sulfide from organic and inorganic sulfur compounds by the action of bacteria, but no investigator appears to have seriously considered the possibility of making practical use of this property of certain bacterial species in the examination of water until in 1894, Schardinger¹ pointed out the advantages in sanitary water examinations of applying tests which would reveal the presence of hydrogen sulfide producing bacteria. Up to this time even search for the presence of members of the colon group of organisms was but seldom practiced in routine work, the procedure usually followed, namely, that of ascertaining merely the number of micro-organisms in a certain definite volume of the sample, Schardinger did not consider to be a reliable criterion of the quality of the water. In searching for methods which would yield more definite information as to the nature and probable source of the bacteria present in the water, he states that he was guided by the investigations of Nencki, in which it was shown that in the small intestine of healthy men, the bacterial processes are chiefly fermentative, but that in the large intestine they are chiefly putrefactive. Since in the great majority of polluted waters we have to deal with fecal contamination there are two groups of bacteria, those causing fermentations and those causing putrefaction, "concerning which one must inform himself in a suspected water."

The method suggested for testing for the presence of putrefactive bacteria consisted in adding 100 cc. of the sample of water to 10 cc. of a sterile solution containing 1 g. Witte peptone and 1 g. sodium chloride. After incubation for twenty-four hours at 37°, a strip of filter paper impregnated with lead carbonate was hung in the neck of the flask.

"If the investigated water was impure, there appeared in a marked degree (a) a pronounced fecal-like odor; (b) the turning of the lead carbonate paper yellow-brown to black, immediately or within a very short time, due to the formation of lead sulfide."

Much work upon "putrefactive" organisms followed, but Schardinger's work appears to have escaped the attention of water analysts until 1897, when Dunham² investigated the Schardinger method and like his predecessors he appears to have been guided by Nencki's work, for he states that

"All sewage which receives human feces contains the bacillus coli communis, or if it does not, has been subjected to germicidal agencies that would also kill pathogenic bacteria, derived from the cases of disease. It is fair to assume that ordinary sewage would also contain the common bacteria of putrefaction. We must therefore direct our attention to the means of demonstrating the presence or absence of those species in the water under examination."

For the detection of "putrefactive" bacteria Dunham made the following slight modification in the Schardinger medium: To about 90 cc. of water, 10 cc. of a 10% peptone, 5% salt solution, previously sterilized,

¹ Schardinger, *Cent. Bakt.*, 16, 853 (1894).

² Dunham, *THIS JOURNAL*, 19, 501 (1897).

were added. This gave a resulting solution containing 1% of peptone and 0.5% of sodium chloride. The mixture was made in a sterile Erlenmeyer flask, provided with a cotton plug. A strip of paper, impregnated with lead carbonate, was suspended over the mixture and the flask was then placed in the incubator at 37° for twenty-four hours. Under these conditions of temperature and nutrition, Dunham claimed that

"The colon bacillus and the bacteria of putrefaction readily multiply and the latter cause the production of hydrogen sulfide which discolours the lead paper."

Although a few water analysts have made use of the Schardinger-Dunham method in the examination of suspected waters, so far as the authors have been able to ascertain no further work has been published upon the subject of the significance of the presence of hydrogen sulfide producing bacteria in drinking waters nor of methods for their detection.

In the course of some ten or more years of experience with this modified method in the hands of the senior author upon many hundred waters, it was found to be of exceeding great value in forming a definite opinion, especially in waters of the class which would have been graded as "suspicious" were only the usual methods followed. The chief drawback was that the indications were not obtained in a short enough time. With badly contaminated waters strong tests for hydrogen sulfide could be obtained in from twenty-four to forty-eight hours, but with other waters from three to four days of incubation were necessary. Moreover, it appeared probable that the hydrogen sulfide rapidly formed was not due to the colon group but to some other class of bacteria, while the slowly evolved hydrogen sulfide might possibly be ascribed to colon group organisms rather than those classed by Dunham as putrefactive.

Part II. Experimental.

Upon studying the data collected, some abnormally short incubation periods were noted and some preliminary work showed that the medium could be sensitized in various ways, and, as the speed with which results can be obtained is a very vital point in the bacteriological examination of water, it was thought that the medium was worthy of a systematic study with a view of obtaining one which would yield positive results in the shortest time and with the greatest possible uniformity.

In the Schardinger medium we have three things which will influence the growth of the bacteria: (1) The concentration of the peptone; (2) that of the inorganic salt present (in this case sodium chloride), and (3) the nature of the reaction of the medium. We may therefore consider that we are dealing with a three-component system and in order to facilitate the investigation the triangular diagram may be resorted to.

The diagram was used in the manner originally proposed by Gibbs and not in the manner later proposed by Roozeboom, which latter is the way in which it is now used by most physical chemists.

By using the diagram according to the Gibbs method, which it will be recalled, gave very excellent results in the hands of Schreiner,¹ in the study of plant nutrients, the concentrations of the three factors, the peptone, inorganic salts, and reaction adjustor could be varied in a systematic manner between wide limits, so as to find the maximum and minimum limits beyond which it would be useless to go in subsequent work, where only one component would be varied at a time. In other words, fields could be found within which the production of hydrogen sulfide would be most rapid and most energetic, and further work confined to those fields.

The rulings of the triangular diagram used gave sixty-six points of intersection and hence in each case sixty-six different combinations of the three components; but in order to obtain combinations in which the salts were high when peptone was low and *vice versa*, and a similar relation of concentrations with respect to acidity recourse must be had to a series of diagrams in which first the order of concentration of one component was reversed, and then another. A series of eight diagrams covers all possible combinations.

It is of course obvious that in each one of the eight diagrams there are a number of points representing possible media which must necessarily be omitted in any given run, as, for example, all those containing no peptone. The actual number of culture media made up in each diagram will therefore never be sixty-six, but will be considerably less than this.

Peptone Used.—The peptone employed was that known as "Witte Peptone" obtained from Kahlbaum. The investigation having extended over a period of three collegiate years, three different lots of peptone were employed. In the case of each shipment, a 10 kilo package was carefully sampled and subjected to chemical and physical tests. The three lots were found to be remarkably uniform and substantially identical in character. But in order to eliminate any possible doubt, simultaneous runs were made on two samples at a time. Identical results were obtained with all three samples in every instance. In addition, it was found desirable to check the compositions by determinations of the acidity, the specific gravity, optical rotation and the coefficient of viscosity of different concentrations of the different samples of peptone at different temperatures. Substantially identical results were obtained.

The chemical analyses of the different samples included moisture, ash, nitrogen, sulfur and phosphates in the ash. The variations in the different samples were no greater than the differences in percentage found in different portions of the same sample.

As is well known, what we ordinarily call a peptone solution is not a solution at all, but is a colloidal suspension, and when peptone is boiled with water there is always formed a heavy sediment which may properly

¹ Schreiner, Bur. Soils, U. S. Dept. Agr., *Bull.* 70.

be considered to be that part of the peptone which is not fine enough to stay in suspension.

In order to ascertain whether this assumption is true and also in order to find out whether any effect would be produced upon hydrogen sulfide production if this sediment were filtered from the medium, the following tests were made:

1. Quantitative determinations were made of the amounts of sulfur, nitrogen, ash, and phosphates in the ash of the sediment and of the peptone. These various constituents were found to be identical within the limits of error of the methods.

2. In each of fifteen of the special culture flasks described below, was placed 10 cc. of unfiltered 30% peptone solution and 0.5 g. of sodium chloride. Another fifteen flasks were similarly prepared, except that filtered peptone solution was used in place of the unfiltered. All of the flasks were plugged and sterilized, and then each was inoculated with 90 cc. of artificial sewage and incubated under similar conditions.

The amounts of hydrogen sulfide produced in the filtered and the unfiltered media were practically identical. It therefore appeared that the precipitate was peptone and that it made no difference whether unfiltered or filtered media were employed. Nevertheless, since it is decidedly advantageous to start with a clear medium so as to detect the growth of bacteria by means of the turbidity and sediment produced in the medium, all peptone solutions were filtered before they were used.

The Witte peptone employed was found to contain 1.006% total sulfur by the Liebig-Koch method,¹ while the peptone in the culture media after filtration was found to contain 0.911% total sulfur, showing that in filtration there is substantially no loss of sulfur.

Koch and Carr² have shown that lipid sulfur compounds are soluble in alcohol, whereas protein sulfur compounds are not. Applying this extraction method to the peptone, two portions were obtained, one soluble in alcohol and one insoluble in this solvent. It was found that the soluble portion contained 0.80% of total sulfur, while the insoluble portion contained 1.08% total sulfur.³

Culture media made from alcohol-soluble peptone and from alcohol-insoluble peptone gave in neither case results as good as those made from the original peptone.

Aqueous solutions of peptone are distinctly acid to phenolphthalein, the amount or degree of acidity rapidly rises with the temperature; hence in adjusting media care must be observed that the media shall always be adjusted at the same temperature. Nor must it be forgotten that

¹ Redfield and Huckle, *THIS JOURNAL*, 38, 607 (1915).

² Koch and Carr, *Ibid.*, 31, 1341 (1909).

³ Redfield and Huckle, *Ibid.*, 38, 612 (1915).

when placed in the incubator the medium becomes more acid than it was at room temperature. After considerable experimentation it was found most convenient to add the reaction adjustor after titrations made at 20°, this being so nearly room temperature as to be readily and quickly obtained. In all the work hereinafter described it will be understood that the stated reactions of the media refers to that at 20°. The acidity of a simple peptone solution or peptone solutions containing simple neutral salts is directly proportional to the concentration.

In the course of some preliminary investigations undertaken some years ago, it was found that the culture flasks employed for testing for the presence of hydrogen sulfide should have wide necks and thus expose a moderate surface of liquid to the air. A 100 cc. modified Pasteur flask was therefore made, having a neck 2 cm. in diameter and of such a size as to bring 100 cc. and 110 cc. levels in the neck of the flask, marks being made for these heights. The small tube of the ground cap was made 4 cm. long and 4 mm. in diameter. This tube serves to hold a cotton plug at its lower end and above the plug a strip of lead acetate paper.

These flasks having answered admirably in routine work were used throughout the present investigation.

After inoculation with a sample, a tin foil cap was placed over the upper end of the tube carrying the lead paper.

As the investigation progressed, evidence was obtained that a better type of flask could probably be devised and further work along this line is being conducted.

The Effect of Peptone Concentration upon Hydrogen Sulfide Formation.—Flasks of media were prepared with the compositions required by the triangular diagram reading clock-wise with concentrations varying between the following limits: 0 to 5% peptone; 0 to 5% acidity in terms of normal hydrochloric acid and 0 to 5% sodium chloride. These runs were made upon reversed diagrams as already described. These flasks were inoculated with equal amounts of sewage¹ and incubated at 38°, and observed at frequent intervals for the first appearance of the blackening of the strips of paper impregnated with lead acetate which had been placed in the tubular top of the caps of the flasks.

It was found in these four runs that the respective fields in which hydrogen sulfide was most quickly developed were as follows:

| | | |
|----------------------|-------------------|---------------------|
| 3.0 to 4.5% peptone, | 0.0 to 1.5% NaCl; | 0.0 to 2.0% N acid. |
| 2.5 to 3.0 | 1.0 to 3.0 | 1.0 to 2.5. |
| 4.0 to 5.0 | 0.0 to 2.5 | 0.0 to 2.5. |
| 4.5 to 5.0 | 2.0 to 2.5 | 2.5 to 3.0. |

¹ In most of the runs an artificial sewage was prepared by adding one loopful (0.02 g.) of fresh human feces to one liter of water, shaking thoroughly and pouring the turbid liquid through a sterile cloth. This water was found to contain 3000 to 5000 organisms growing on gelatin at 26°, 100 to 200 colonies on agar at 38°, of which from 20 to 40 were of the *B. coli* group.

From a careful study of all of the data obtained in the four runs, it was found that the very best conditions had been obtained within the following limits:

2.5 to 5.0% peptone; 0.5 to 1.5% NaCl; 0.5 to 1.5% *N* acid.

Consequently a run was now made, in which all of the possible combinations of 2.0%, 2.5%, 3.0%, 3.5% and 4.0% of peptone; 0.5%, 1.0% and 1.5% of NaCl; and 0.5%, 1.0% and 1.5% of normal acid were used, plotted on two component diagrams.

Four checks with 2.0%, 2.5%, 3.0% and 4.0% of peptone, with no added salt and with a reaction of 1.0% normal acid were also prepared.

It was found in the uninoculated media, that of the combinations prepared, the only ones which were clear, with very little sediment, were those containing 3.0% of peptone, 1.0% and 1.5% of NaCl, and with an acidity to phenolphthalein of 1.5% normal acid. It was, moreover, a general rule that the quantity of peptone and of sodium chloride did not seem to have much influence on the amount of turbidity in the solution, but that the reaction did have such an influence; the less the acidity, the greater the turbidity; but there were many exceptions.

Each flask was inoculated with 90 cc. of artificial sewage.

As regards the turbidity of the inoculated media before incubation, none were perfectly clear, with no sediment, but the best combinations were those in which the reaction was equivalent to 0.5% normal acid, and where NaOH had been used to adjust the reaction.

The inoculated flasks were incubated at 38° and frequently observed for evidences of hydrogen sulfide production.

As regards the rapidity of hydrogen sulfide production, it was found to be most rapid in those combinations containing 3.5 and 4.0% of peptone, the concentration of the sodium chloride and the reaction of the media apparently not making a great deal of difference, in the narrow limits used.

The largest amounts of hydrogen sulfide were produced in general in the flasks having from 3.0% to 4.0% of peptone; from 0.5% to 1.5% of NaCl; and with a reaction equivalent to from 1.0% to 1.5% normal acid. These were also the combinations in which the media became the most turbid after incubation and in which the largest amounts of grayish green sediment were produced. It was also noted that in most of these flasks, there were particles of dark green material floating on the surface which sank on tapping the flasks.

In order to obtain more reliable information as to which combinations were really best and produced hydrogen sulfide most rapidly, it was deemed advisable to make up in triplicate those combinations which had given the best results. While none of the combinations used were perfectly clear and free from sediment either before or after inoculation, they were

near enough so for all practical purposes, so far as judging how the growth and development of the bacteria had proceeded on incubation.

The results of all the combinations tried showed that when sodium chloride was the inorganic salt present, there was not much choice between 3.0%, 3.5% and 4.0% of peptone, all of which were much superior to 2.0% and 2.5% of peptone.

In order to throw light upon the question of the effect of the inorganic salt upon the peptone concentration, runs were made, similar in all respects to those recorded above but with the difference that sulfate, nitrate and phosphate of sodium were substituted for sodium chloride; and also in which the chloride, sulfate, nitrate and phosphate of potassium, of ammonium, of calcium and of magnesium were, respectively, substituted for sodium chloride and in which the reaction was adjusted in a variety of ways.

Without giving the details of the results of each run, suffice it to say that in all cases from 3.0% to 4.0% of peptone furnished the best concentrations for most rapid and most energetic production of hydrogen sulfide by the bacterial floras employed. The value of the inorganic salt in the medium will be discussed below.

In most standard culture media it is customary to add an extract of fresh lean beef as one of the components. It was therefore thought essential that the value of such an addition to the Schardinger medium be investigated. To this end fifty flasks were prepared in which varying volumes of meat broth were added. The meat broth used was prepared by digesting 2100 g. of finely chopped beef with 4200 cc. of water. The extract was filtered through cloth and the meat pressed in an iron press until substantially dry. The extract was then boiled, made neutral to phenolphthalein with sodium hydroxide and filtered through paper. The clear meat extract thus obtained contained 2.22% of total solids of which 0.69% was ash. The fifty flasks employed were divided in lots of ten of similar concentration, with respect to meat extract and peptone. Each set of ten was again subdivided, half receiving 0.5% of potassium chloride, the other half no potassium salt. The series after inoculation contained from 0 to 3% peptone and from 0 to 50 cc. meat extract. The 3% peptone contained no meat extract and the 50 cc. meat extract flasks no added peptone, between these two limits the media contained variable quantities of each nitrogenous component. In every case the volume of the media was 65 cc. and to this was added 35 cc. of sewage. At the end of eighteen hours all of the flasks containing meat broth had begun to show hydrogen sulfide, while those containing peptone, but no meat, had not yet developed a test. At the end of twenty-four hours the simple peptone media had begun to show hydrogen sulfide, but the media containing meat broth still showed more. The most powerful evolution

occurred in media containing 2.25 g. of peptone and 50 cc. of meat extract. In all the media in this run the presence of the potassium chloride led to more rapid production of hydrogen sulfide and in larger amounts.

Were conclusions to be based merely upon the time of the appearance of hydrogen sulfide as revealed by the lead acetate paper, it would appear that the medium was greatly improved by the addition of the meat extract. Subsequent investigations and a careful study of data showed that, just as with peptone alone, concentration played an important role. Extracts made with meat purchased at different times were found to be variable in composition and therefore could not be relied upon as yielding media of reliable uniformity and concentration with respect to the sulfur containing body or bodies. The media in all of the flasks containing beef extract remained yellow in color even after much hydrogen sulfide had been produced, and what little sediment was present was light yellow in color, while the 3.0% peptone, 0.5% potassium chloride media all turned turbid and green with dark green sediment and dark green floating cakes. This color reaction, joined to an intense fecal odor in the peptone media, constitutes a most valuable indication that the water being tested is seriously contaminated—indications which are usually lost when meat extract is present. It therefore appeared probable that the slight shortening of the period required for the first appearance of hydrogen sulfide was more than outweighed by the greater labor involved and by the loss of valuable diagnostic features.

Further study of the addition of meat broth was abandoned and a study of other possible sensitizing agencies was attempted.

The Influence of the Addition of Inorganic Salts.—Both Schardinger and Dunham recommended the addition of sodium chloride to their culture media. In fact, the addition of this salt to culture media has been quite uniformly practiced by bacteriologists. A careful search of the literature failed to disclose any data upon which a reliable opinion could be based as to the actual influence of this compound, nor evidence that the quantities employed were the best concentrations for the ends in view.

That some inorganic salts in the media were desirable, there was no question, for it had long before been found by one of us that media made up with water from the University water supply gave better results than when made from distilled waters so far as their applicability to the examination of at least the natural waters of the East Central United States. "Tap" water was therefore invariably employed in making up all media.

A study of the data yielded by the runs on the triangular diagrams already tried showed that the presence of sodium chloride was highly desirable.

The problem we next set ourselves was that of ascertaining whether sodium chloride was the best salt to use and the influence of varying con-

centrations of the different salts tried. A series of runs was made in which sodium sulfate, sodium nitrate, potassium chloride, magnesium chloride calcium chloride and ammonium chloride were, respectively, substituted for the sodium chloride.

Advantage was taken of the experience which had been gained in making the runs with sodium chloride, so that with a simple change in the arrangement of the diagram, it was possible to gain as much information from the use of one triangular diagram for each of these salts as had been obtained from running four separate diagrams with sodium chloride. The modified diagram read in a clock-wise direction in the following manner: 1.0 to 6.0% peptone; 5.0 to 0.0% *N* acid; 5.0 to 0.0% salt.

Starting with 1.0% peptone instead of 0.0% had the following advantages: It eliminated the 0.0% and 0.5% peptone solutions which were obviously worthless and it placed the 2.5%, 3.0% and 0.5% peptone solutions in that part of the diagram where the concentrations of salt and acidity had been found to be the best suited to good growth and hydrogen sulfide production.

In the previous runs the peptone had been weighed out for each concentration desired, but from this time on proportional amounts of 30% peptone solutions were used. This had the advantage of using the same identical solution of peptone for all of the inoculations and also of making the uninoculated media of larger volume, thereby better keeping all of the components in solution.

In all of these runs, the same check solutions were used in order to make them as nearly comparable as is possible whenever a fresh lot of sewage must be prepared for each run. These check solutions had the following compositions:

| | | |
|--------------|-----------|--------------------|
| 3.0% peptone | 0.5% NaCl | 1.5% <i>N</i> acid |
| 3.5% | 1.0% | 1.3% |
| 4.0% | 1.5% | 1.5% |
| 3.0% | 0.5% | 1.02% (unadjusted) |

After inoculation the results obtained with these checks were always similar in character.

The best results obtained with the other media containing the different inorganic salts were as follows:

Sodium chloride from 0.5 to 1.5%, more than 1.5% inhibiting; sodium sulfate from 0.5 to 1.5%, more than 1.5% inhibiting; potassium chloride from 0.5 to 3.0%, required more than 3% to inhibit; magnesium chloride from 0.5 to 1.0%, more than 2% inhibiting; calcium chloride from 0.5 to 2.0%, more than 2% inhibiting; ammonium chloride from 0.0 to 1.5%, more than 2% inhibiting.

The results of these runs seemed to indicate that potassium chloride was the best of the salts tried and that its addition to the media was decidedly advantageous. Nevertheless it was felt that more evidence was

essential before a reliable opinion could be formed and especially did it seem necessary to try as many different combinations as possible of basic and acid ions.

As the net results of some eight hundred runs already made the optimum conditions for the formation of hydrogen sulfide appeared to be in media having a peptone content of 3% and an acidity equivalent to from 1.0 to 1.5% normal acid. It was further found that, when this acidity was obtained from the unneutralized natural acidity of the peptone itself, the results appeared to be a little better than when obtained through the addition of an acid after neutralization with an alkali; in all such cases due allowance being of course made for the increased amount of inorganic salt thus introduced.

Although, as stated above, after a large amount of data had been collected, it was found that just as good and in most cases, better results were obtained when using an unadjusted 3% peptone medium, of which the reaction was always about 1.02% of normal acid; still in the early part of the work many experiments were tried to find the best reaction, and such bases as sodium hydroxide, potassium hydroxide, ammonium hydroxide, calcium oxide and magnesium oxide, and such acids as hydrochloric, sulfuric and nitric were used in adjusting the reaction to neutrality and also to various degrees of alkalinity and of acidity; in combination with various salts and also with no added inorganic salts.

As a result of the data collected in this connection in about five hundred inoculations, sodium hydroxide and potassium hydroxide proved to be the best alkalis to use, with little choice between them, due presumably to the very small amounts of basic elements which were introduced in adjusting the reactions. Hydrochloric acid proved to be the best of the acids. Nitric acid, as would naturally be expected, proved a positive detriment.

When peptone, potassium chloride, hydrochloric acid and potassium hydroxide were used in preparing the media, good results were obtained in some two hundred inoculations over a much wider field than with any other combination, as has already been noted; very good and quick results having been obtained with concentrations of acidity from 0.5% to 3.0%, inclusive, but the very best results were obtained when the acidity was from 1.0% to 1.5% with very little choice between these concentrations, the preference, if any, being for 1.5%. This preference, however, was so slight that it is outweighed by the greater simplicity of leaving the reaction unadjusted at about 1.02%, when 10 cc. of 30.0% peptone is used in 100 cc. of inoculated media.

The limits for the best concentrations of initial acidity for salts other than potassium chloride were found to be as follows, the titrations being made at 20°:

| | |
|---------------------------------------|--|
| For NaCl, | from 0.0% to 2.0% <i>N</i> acid, best at 1.0%. |
| For Na ₂ SO ₄ , | from 0.5% to 1.0% <i>N</i> acid, best at 0.5%. |
| For MgCl ₂ , | from 0.5% to 1.5% <i>N</i> acid, best at 1.0%. |
| For CaCl ₂ , | from 1.0% to 2.0% <i>N</i> acid, best at 1.5%. |
| For NH ₄ Cl, | from 1.0% to 1.5% <i>N</i> acid, best at 1.0%. |
| For K ₂ SO ₄ , | from 0.5% to 2.0% <i>N</i> acid, best at 1.0%. |

Having thus established the limits for acidity, runs were made in which the variable component was the inorganic salt. Concentrations of 0.5, 1.0 and 1.5% of the following salts were tried: NaCl, KCl, NH₄Cl, CaCl₂, MgCl₂, Na₂SO₄, K₂SO₄, (NH₄)₂SO₄, CaSO₄, MgSO₄, NaNO₃, KNO₃, NH₄NO₃, Ca(NO₃)₂, Mg(NO₃)₂. Two check flasks were also prepared containing no added salts.

The quickest and most abundant evolution of hydrogen sulfide was obtained in the media containing 0.5 and 1.0% KCl; 0.5 and 1.0% NaCl; 0.5% K₂SO₄; 0.5% CaSO₄; 1.0 and 1.5% MgSO₄. Again considerably the best results were obtained with KCl. The nitrates all showed a marked inhibiting action.

The five salts which were found to yield the best results were again tried, but in narrow limits of concentration, 0.25, 0.50, 0.75 and 1.0%. Again the best results were obtained with KCl in concentrations of 0.50 and 0.75%, with NaCl next in order. The areas upon the triangular diagram enclosing the best concentrations for these five salts are shown in Fig. 1.

Phosphates were not included in the tables on account of the fact that preliminary trials had already indicated that they were of little, if any, value and probably objectionable. It seemed nevertheless wise to study their effect separately. The following salts were tried, with the results indicated: H₂KPO₄ in concentrations in the finally inoculated media of from 0.0 to 1.5%. Peptone, 3%; acidity, 1.2%. All the solutions precipitated badly. When sterilized, those containing the highest proportions were practically turbid jellies before inoculation. None of the series developed hydrogen sulfide at the end of twenty-four hours and only a few at the end of seventy-two hours. Of the checks with KCl and NaCl the former gave the most rapid and abundant evolution of the gas.

The marked inhibiting effect of this salt is probably not necessarily due to the PO₄ ion, since the acidity from a 0.5% solution was found to be as high as 5.0% in terms of normal HCl. It is manifestly impossible to reduce this acidity to an equivalent of between 1 and 1.5% (the optimum acidity previously found), since the addition of an alkali would necessarily change the nature of the phosphate added. HNa₂PO₄, HK₂PO₄, HMgPO₄, HCaPO₄, H(NH₄)₂PO₄, HKNH₄PO₄, HNaNH₄PO₄, these salts were introduced into peptone solutions, unadjusted in amounts such that the inoculated media would contain 0.05, 0.15 and 0.25% of the basic element present in the salts. The added concentrations equivalent to the best

concentrations obtained with NaCl and KCl. These salts were thus calculated because it had been previously found that it was the potassium or sodium ions which appeared to be beneficial and that the acid ion, so far as Cl and SO_4 are concerned, had little effect. As checks, media containing KCl, K_2SO_4 and NaCl, respectively, were prepared with the K and Na ions present in the proportion 0.05, 0.15 and 0.25%. Other checks contained no added inorganic salt.

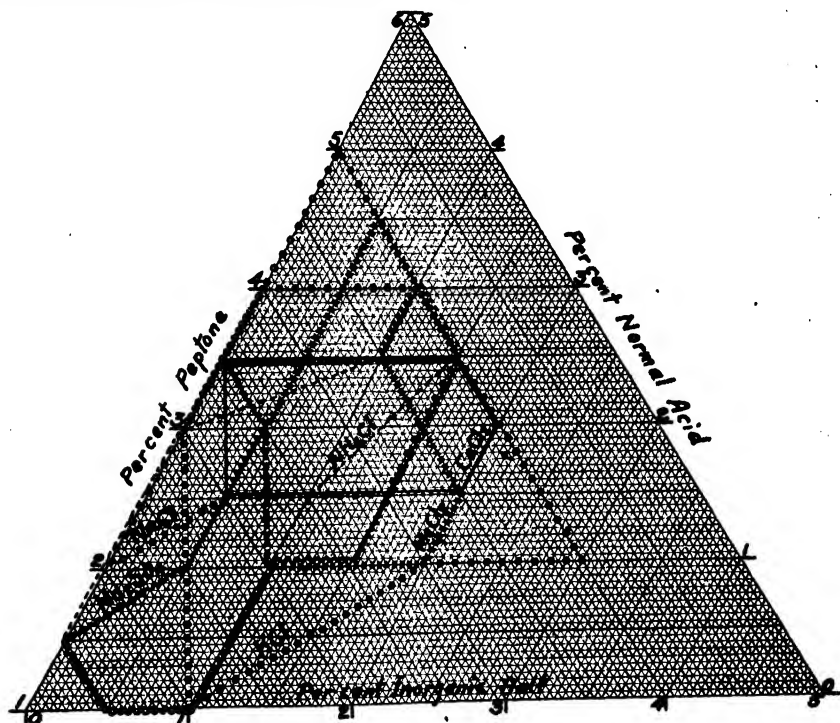


Fig. 1.

Upon sterilizing the phosphate containing media it was found that considerable hydrogen sulfide resulted from a chemical reaction between these salts and the peptone. The largest quantity of this chemically formed hydrogen sulfide appeared in media containing ammonium phosphate, and least in those containing magnesium phosphate.

None of the phosphate containing media gave as good results as the check flasks, while of these the media containing KCl prove to be superior to the others. Of the phosphated media those with HMgPO_4 were better than the others, then followed HNaKPO_4 , HK_2PO_4 , $\text{HNNH}_4\text{KPO}_4$, HNa_2PO_4 , HCaPO_4 , $\text{HNaNH}_4\text{PO}_4$, $\text{H}(\text{NH}_4)_2\text{PO}_4$.

The influence of tertiary (normal) phosphates was next investigated.

Media were prepared in which were introduced an amount of the basic ion equivalent to that found to have given the best results with KCl. In these runs the following salts were tried: $Mg_3(PO_4)_2$, $Ca_3(PO_4)_2$, NH_4MgPO_4 , Na_3PO_4 , K_3PO_4 , KNa_2PO_4 and NaK_2PO_4 . Check flasks with NaCl and KCl were inoculated and incubated at the same time.

In the media containing the phosphates only traces of hydrogen sulfide were formed, while all the checks developed large amounts.

In order that the influence of moderate amounts of phosphates should be studied in all its phases, media were next prepared in which in addition to the phosphates some received KCl, some NaCl and some K_2SO_4 . In these media only those containing HK_2PO_4 and KCl yielded appreciable traces of H_2S .

In all of the trials made with phosphates more than mere traces exerted a decidedly deleterious effect so far as the formation of hydrogen sulfide was concerned. As has already been stated part of this deleterious action is unquestionably due to too high an acidity. Although any addition of a compound which would reduce this acidity would necessarily change the character of the phosphates present and probably result in undesirable precipitates, it was decided to try the effect of the addition of a little finely divided $CaCO_3$. Moreover, it had been found that the final acidity to phenolphthalein was about 3.0% in those flasks of media in which much hydrogen sulfide was produced. This is doubtless due to the decomposition of the peptone into simpler amino, or other organic acids. The question naturally arose "Is it not possible that if some carbonate, which itself will not effect the reaction of the medium but which will tend to neutralize the acid products of bacterial activity, is introduced, that by so neutralizing these by-products it may materially aid the bacteria in producing hydrogen sulfide?" Calcium carbonate was first tried and was introduced to the amount of 0.5% in combination with the following:

| | | | |
|--------|----|---------------------|-----------------------|
| 0.25% | K | from KCl. | |
| 0.25% | Na | from NaCl. | |
| 0.25% | K | from K_2SO_4 . | |
| 0.20% | K | from KCl and 0.05% | K from K_2HPO_4 . |
| 0.15% | K | from KCl and 0.10% | K from K_2HPO_4 . |
| 0.175% | K | from KCl and 0.075% | K from K_3PO_4 . |
| 0.10% | K | from KCl and 0.15% | K from K_3PO_4 . |
| 0.225% | K | from KCl and 0.025% | K from KH_2PO_4 . |
| 0.20% | K | from KCl and 0.05% | Na from Na_2HPO_4 . |
| 0.15% | K | from KCl and 0.10% | Na from Na_2HPO_4 . |

There was a heavy sediment of insoluble calcium carbonate present throughout the run, which is an undesirable feature as it renders difficult, if not impossible, the formation of an opinion as to the character of the growth in the cultures.

As a result of the run, it was found that hydrogen sulfide was developed rapidly and in large amounts in just about as many flasks that contained no carbonate as was the case when the carbonate was present, leading to the conclusion that calcium carbonate has no beneficial influence on the production of hydrogen sulfide by bacteria.

Before abandoning the addition of carbonates it was deemed advisable to try a soluble carbonate and, as it was desired to use one which would least influence the reaction of the medium to phenolphthalein, sodium bicarbonate was chosen. The carbonate, in amount sufficient to give a concentration of 0.25% in the final inoculated medium, was used in combination with potassium chloride, sodium chloride and potassium sulfate, respectively, each of these salts being used in amounts to give 0.25% of the basic element present. As controls, flasks were prepared in triplicate containing 0.25% sodium bicarbonate without other salt; and with 0.25% of basic element furnished by potassium chloride, sodium chloride and by potassium sulfate without any sodium bicarbonate being present; and also three flasks containing no added salt.

As the result of the run, it was found that after sterilization and before inoculation, all of the flasks containing the added carbonate showed an undesirable, slight turbidity, and a marked deposit in the form of an adherent white film on the glass. This deposit, after thorough washing, was tested microchemically and proved to be calcium carbonate in the form of spherocrystals of minute size. After the flasks had been inoculated and incubated, this film still persisted, being slightly augmented. A quantitative determination of the amount of calcium carbonate was made by titrating hot with 0.1 *N* hydrochloric acid, using ethyl orange as the indicator and it was found to be equivalent to 0.33%.

As far as the production of hydrogen sulfide was concerned, the results were very markedly against the use of sodium bicarbonate, as only one flask containing it showed even a trace of hydrogen sulfide produced. Moreover, when sodium bicarbonate was present, there was no greening of the solution or formation of dark green or grayish green sediment or cakes. The control flasks containing no sodium bicarbonate all produced hydrogen sulfide quickly and in large quantities, those containing potassium chloride giving the best results.

The reaction of those media not containing the carbonate when they showed a trace of hydrogen sulfide production, was about 0.70% normal acid on the average, using phenolphthalein as indicator, while the average reactions in the flasks which contained the sodium bicarbonate was 1.68% normal acid when showing a like amount of hydrogen sulfide. It may be concluded from these figures that it is erroneous to suppose that the presence of a carbonate would be beneficial by reason of the neutralizing effect which it would have upon the acid reacting substances

set free by the bacteria, thus removing from the field the by-products of bacterial life which it was thought might have an inhibiting influence on the development of the bacteria and the consequent production of hydrogen sulfide. Quite to the contrary, they proved that the bacteria must first neutralize this carbonate and then develop an acidity to phenolphthalein of 1.68% normal acid in the solution before they could begin breaking down the sulfur compounds of the peptone to yield hydrogen sulfide.

That hydrogen sulfide had not been produced and then held in solution as sodium sulfide, potassium sulfide, ferrous sulfide or calcium sulfide was demonstrated by the fact that no appreciable amounts of hydrogen sulfide could be detected upon acidifying a number of the cultures with hydrochloric acid.

During the course of the work, and more especially, while making titrations of some of the media after incubation, it was noted that there would be at times a very rapid evolution of hydrogen sulfide. This never occurred during the first twenty-four hours of incubation, and never, as far as observed, before the cultures had reached an acidity of 3.0%.

The evolution was so rapid at times that from one-quarter to one-third of the lead acetate papers in the tubes of the culture flasks would be blackened in the half hour, or so, that it took to titrate a group of fifteen or twenty cultures.

It was also noted that the same thing occurred in the incubator in short periods of time.

In order to try out the method with waters of a varying degree of pollution, an artificial sewage was prepared and plated on standard gelatin and on standard agar on lactose-litmus agar and also inoculated into fermentation tubes containing a 2.0% dextrose, 3.0% peptone, 0.5% potassium chloride medium.

After forty-eight hours of incubation, the gelatin plates showed 2800 colonies per cc. with 20 *B. coli communis* per cc., and the agar plates showed 200 colonies per cc. Of the fermentation tubes, those which had been inoculated with 1 cc. and with 0.1 cc. had one-half of the closed arms filled with gas, but those inoculated with 0.01 cc. and 0.001 cc. showed no signs of gas or growth.

For inoculating the media for the detection of hydrogen sulfide, dilutions of the sewage of 5 : 100, 10 : 100, 15 : 100, 20 : 100, 25 : 100, 30 : 100, 35 : 100, 40 : 100, 45 : 100, 50 : 100, 55 : 100, 60 : 100, 65 : 100, 70 : 100, 75 : 100, 80 : 100 and 85 : 100 were made with sterile tap water, and the flasks inoculated with these dilutions were incubated at from 37-38°.

There was, as would be expected, a gradual increase in the amounts of hydrogen sulfide produced and also in the rapidity with which it was produced as the concentration of the sewage was increased, but after eigh-

teen hours of incubation, the sewage which had been reduced to 85 : 100 had given an appreciable amount of hydrogen sulfide with a turning green of the medium and turbidity produced therein; and after thirty hours, much hydrogen sulfide had been produced with a dark green sediment and dark green floating cakes and an accumulation of gas at the top of the solution by even the 10 : 100 dilution; so it may be concluded that a positive test will be given in eighteen hours with a 90 cc. inoculation of a water which would show 2380 colonies per cc. on standard gelatin with 17 *B. coli* per cc.; 170 colonies on standard agar; and gas in dextrose, peptone, potassium chloride medium in fermentation tubes with a 1 cc. inoculation; while a positive test will be given in thirty hours with a water containing only about one-eighth of this amount of pollution, with a proportionate amount of time required by degrees of pollution between these extremes.

These figures are well within the limits of what will be found in sewage polluted waters and hence the method of detecting sewage pollution in a water by means of the hydrogen sulfide produced in the proposed medium by the putrefactive organisms, affords a very valuable method for augmenting and helping to interpret the data obtained by the chemical and bacteriological examinations of water samples.

In order to ascertain whether the feces of domestic animals contributed to contaminated waters bacteria which produce hydrogen sulfide, and in what relative amounts, the following experiments were made:

Into one liter of filtered water taken from the University service pipes there was introduced one loop full (0.02 g.) of the feces of the animal selected for study. Two series of culture flasks were prepared; in each case such that when ready for incubation a final volume of 100 cc. would be obtained containing 3% of Witte peptone, 0.5% potassium chloride, and would have an acidity a trifle over 1.0%. One series contained 90 cc. of culture media, the other 10 cc.; to the first series 10 cc. of the above described artificially contaminated water, and to the second 90 cc. were slowly added.

The results obtained can best be shown by Table I.

It will be seen that in every case hydrogen sulfide was eventually produced, but that in the case of the horses, cows, and sheep, the formation of this compound was slow, only traces being formed under thirty-six hours. Should further investigations substantiate these results their importance in the interpretation of the formation of much hydrogen sulfide in eighteen to twenty-four hours in the case of contaminated waters is not to be ignored.

It was thought essential that the investigation be extended to include a study of the action of pure cultures of the *B. coli* group. We had available thirty-four strains and substrains of organisms believed to be

TABLE I.

| Amount inoculated, and kind. | Millimeters blackened of lead acetate papers in | | | | |
|---------------------------------|---|---------|---------|---------|---------|
| | 18 hrs. | 21 hrs. | 24 hrs. | 36 hrs. | 48 hrs. |
| 10 cc. human..... | 0 | 0 | 0 | 4 | 12 |
| 90 cc. human..... | 0 | 1 | 5 | All | All |
| 10 cc. cow, I..... | 0 | 1 | 2 | 10 | All |
| 90 cc. cow, I..... | 0 | 0 | 0 | 8 | All |
| 10 cc. cow, II..... | 0 | 0 | 0 | 12 | All |
| 90 cc. cow, II..... | 0 | 1 | 4 | All | All |
| 10 cc. calf, I..... | 0 | 1 | 4 | All | All |
| 90 cc. calf, I..... | 2 | 5 | 8 | All | All |
| 10 cc. horse, I..... | 0 | 0 | 0 | 14 | All |
| 90 cc. horse, I..... | 0 | 0 | 1 | 6 | All |
| 10 cc. horse, II..... | 0 | 0 | 0 | 14 | All |
| 90 cc. horse, II..... | 0 | 0 | 1 | 5 | 20 |
| 10 cc. pig, I..... | 0 | 0 | 0 | 17 | All |
| 90 cc. pig, I..... | 0 | 0 | 1 | 15 | All |
| 10 cc. pig, II..... | 0 | 1 | 2 | 16 | All |
| 90 cc. pig, II..... | 0 | 1 | 4 | All | All |
| 10 cc. sheep, I..... | 0 | 0 | 1 | 8 | All |
| 90 cc. sheep, I..... | 0 | 0 | 0 | 6 | 20 |

B. coli which had been isolated from contaminated waters and sewage. These thirty-four strains were being employed in the study of carbohydrate media and were taken for use from a series of tubes of Harrison's esculin bile medium and from a series of fermentation tubes of Stokes' neutral red medium. This gave sixty-eight strains or substrains in all. These were inoculated in different bacterial dilutions into media whose final incubated concentrations were 3% peptone, 0.5% potassium chloride, acidity 1.02%. The results obtained were as follows:

- 18 hours, 1 culture had begun to develop hydrogen sulfide.
- 24 hours, 5 cultures had begun to develop hydrogen sulfide.
- 36 hours, 7 cultures developed H₂S, two of them moderate amounts.
- 48 hours, 9 cultures developed H₂S, two of them moderate amounts.
- 4 days, 26 cultures developed H₂S, four of them moderate amounts.
- 5 days, 43 cultures developed H₂S.
- 6 days, 47 cultures developed H₂S.
- 7 days, 49 cultures developed H₂S.
- 8 days, 52 cultures developed H₂S while 16 still showed none.

Although the authors do not consider that these results are conclusive, they do believe that taken in conjunction with the results of the runs made upon animal feces and those obtained from the examinations of contaminated waters, the production of large quantities of hydrogen sulfide in from eighteen to twenty-four hours is to be regarded as indicative of the presence of organisms other than *B. coli*¹ and there appears

¹ This is further substantiated by the work of Kendall, Day and Walker, THIS JOURNAL, 35, 1201 (1913), who find that the proteolytic activity of the *B. coli* group is relatively very low and slow.

to be good grounds for the use of the term "putrefactive bacteria" in water examinations as suggested by Schardinger and by Dunham.

Some evidence has also been obtained by the authors that in a mixed flora the formation of hydrogen sulfide is more rapid than from the isolated pure cultures.

If, therefore, tests for hydrogen sulfide production are to be made in water examinations the analyst must take into account the rate and the amount of this gas formed and the time of its first appearance.

In the course of the investigation a number of purely biochemic questions and problems arose upon which considerable time was spent such as, for example, the actual source of the hydrogen sulfide evolved, whether from firmly or loosely bound sulfur compounds, the actual quantity formed, the rate of formation, the influence of the presence of oxygen, etc. Some of these questions have already been alluded to, but although interesting, appear to have no direct bearing upon the sanitary significance of hydrogen sulfide production. The influence of oxygen, however, needs more than a passing word of comment. It is generally stated in most text-books of microbiology, that hydrogen sulfide is formed by a reducing reaction and therefore the most favorable conditions should be

TABLE II.—SURFACE WATERS.

| Source of sample. | Month of year. | Quality from chem. anal. | Colonies per cc. on | | Gas producers. | Colon group present in | | | Indol production. | Hydrogen sulphide production. |
|-------------------|----------------|--------------------------|---------------------|--------------|----------------|------------------------|-------|--------|-------------------|-------------------------------|
| | | | Agar 38°. | Gelatin 20°. | | 1 cc. | 5 cc. | 10 cc. | | |
| Spring brook | Jan. | Good | 50 | 6 | + | — | — | ? | + | ++ |
| River | Jan. | Bad | 25 | 79,000 | + | + | + | + | + | + |
| Filtered river | Jan. | Good | 2 | 460 | — | — | — | — | + | ++ |
| Creek | Mar. | Poor | .. | 460 | + | + | + | + | + | ++ |
| River | Mar. | Poor | 3 | 2,200 | — | — | — | — | + | Trace |
| Creek | May | Poor | 1 | 300 | — | — | — | — | Trace | Trace |
| Ditch* | July | | 700 | 120 | — | — | — | — | — | — |
| Ditch | July | | 500 | 2,500 | + | + | + | + | +++ | +++ |
| Ditch | July | | 3,000 | 17,000 | + | — | — | + | + | +++ |
| River | Aug. | Poor | 1,000 | 2,100 | + | — | — | — | ++ | +++ |
| Lake | Aug. | Good | 30 | 370 | + | — | — | — | ++ | ++ |
| Filtered river | Aug. | Poor | 12,000 | 375,000 | + | ? | + | + | +++ | + |
| River | Aug. | Bad | 1,000 | 2,100 | + | ? | + | + | +++ | +++ |
| Filtered river | Sept. | Good | 3 | 40 | + | — | — | ? | + | +++ |
| Spring brook | Oct. | Suspicious | 6 | 70 | + | — | ? | + | + | +++ |
| River | Oct. | Bad | 80 | 600 | + | + | + | + | +++ | +++ |
| River | Oct. | Bad | 200 | 1,600 | + | + | + | + | +++ | ++ |
| Reservoir | Oct. | Suspicious | 20 | 400 | + | ? | + | + | + | +++++ |
| River | Dec. | Poor | 160 | 1,600 | + | — | + | + | +++ | + |
| River | Dec. | Suspicious | 75 | 4,600 | + | — | ? | + | +++ | +++ |
| Filtered river | Dec. | Suspicious | 1 | 8 | — | — | — | — | + | ++ |
| River | Dec. | Bad | 60 | 50,000 | + | + | + | + | + | ++ |
| Filtered river | Dec. | Poor | 35 | 5,000 | + | — | — | ? | + | + |

* Hot from exhaust steam from steam pump.

those in which the growth of the organisms producing this reaction takes place in the presence of a minimum amount of oxygen. It is obvious that this has a direct bearing upon the testing for the presence of hydrogen sulfide forming bacteria in water and required investigations. The details of the work done need not be here discussed. In all the experiments made, quantitative analyses showed that more hydrogen sulfide was evolved and less sulfur remained in the peptone culture media if air was present than if it was absent when using a mixed sewage flora. The largest quantities of hydrogen sulfide were obtained when a slow current of sterile air was passed over the surface of the liquids in the culture flasks. Actually 100% more total sulfur was thus converted into hydrogen sulfide.

TABLE III.—SPRING WATERS.

| Month of year. | Quality from chem. anal. | Colonies per cc. ou | | Gas producers. | Colon group present in | | | Indol production. | Hydrogen sulphide production. |
|----------------|--------------------------|---------------------|--------------|----------------|------------------------|-------|--------|-------------------|-------------------------------|
| | | Agar 38°. | Gelatin 20°. | | 1 cc. | 5 cc. | 10 cc. | | |
| Jan. | Good | 1 | 40 | — | — | — | — | — | — |
| Jan. | Good | 13 | 7,200 | — | — | — | — | ++ | +++ |
| Feb. | Good | 4 | 110 | — | — | — | — | + | +++ |
| Feb. | Good | 4 | 95 | + | — | — | ? | Trace | +++ |
| Mar. | Poor | 0 | 15 | + | — | — | — | Trace | — |
| May | Good | 1 | 140 | + | — | — | — | — | — |
| June | Suspicious | 30 | 3,000 | + | — | + | + | + | + |
| June | Good | 1 | 35 | — | — | — | — | — | — |
| June | Poor | 12 | 350 | + | + | + | + | ? | — |
| July | Suspicious | 3 | 500 | — | — | — | — | — | — |
| July | Bad | 2 | 170,000 | + | — | ? | + | + | ++ |
| Aug. | Suspicious | 65 | 65 | + | — | — | — | Trace | Trace |
| Aug. | Bad | 450 | 120,000 | + | + | + | + | + | +++ |
| Aug. | Good | 70 | 10,000 | + | + | + | + | ? | Trace |
| Aug. | Good | 22 | 600 | + | ? | + | + | Trace | — |
| Aug. | Good | 190 | 15,000 | — | — | — | — | — | — |
| Aug. | Good | 600 | 3,500 | + | — | — | — | + | + |
| Aug. | Good | 30 | 350 | + | + | + | + | Trace | Trace |
| Sept. | Bad | 20 | 150 | — | — | — | — | — | — |
| Sept. | Bad | 0 | 10 | — | — | — | — | — | — |
| Sept. | Poor | 1,900 | 390 | + | — | — | + | + | ++ |
| Oct. | Good | 15 | 40 | + | — | — | ? | — | — |
| Oct. | Bad | 3 | 210 | + | — | — | ? | — | — |
| Oct. | Good | 20 | 800 | — | — | — | — | ++ | + |
| Oct. | Good | 15 | 730 | + | — | ? | + | +++ | + |
| Oct. | Poor | 0 | 90 | — | — | — | — | — | — |
| Dec. | Good | 70 | 180 | — | — | — | — | Trace | Trace |
| Dec. | Good | 0 | 9 | + | — | — | — | — | — |
| Dec. | Good | 1 | 3 | — | — | — | — | — | Trace |
| Dec. | Good | 0 | .8 | — | — | — | — | Trace | Trace |
| Dec. | Good | 2 | 150 | + | ? | ? | + | ++ | +++ |
| Dec. | Good | 0 | 12 | — | — | — | — | + | Trace |

TABLE IV.—WELL WATERS.

| Kind of well. | Depth in feet. | Month of year. | Quality from chem. anal. | Colonies per cc. on | | Gas producers. | Colon group present in | | | Indol production. | Hydrogen sulfide production. |
|---------------|----------------|----------------|---------------------------|---------------------|--------------|----------------|------------------------|-------|--------|-------------------|------------------------------|
| | | | | Agar 38°. | Gelatin 20°. | | 1 cc. | 5 cc. | 10 cc. | | |
| Artesian | 303 | Jan. | Good | 0 | 5 | — | — | — | — | — | Trace |
| Artesian | 286 | Jan. | Good | 1 | 7 | — | — | — | — | — | — |
| Artesian | 280 | Jan. | Good | 3 | 3 | — | — | — | — | ? | + |
| Artesian | 276 | Jan. | Good | 0 | 6 | — | — | — | — | — | — |
| Artesian | 295 | Jan. | Good | 0 | 2 | — | — | — | — | — | — |
| Drilled | 342 | Jan. | {Cl = 312 Solids 4200} | 400 | 350 | + | — | — | ? | Trace | ++ |
| Driven | ... | Feb. | Bad | 95 | 225 | + | + | + | + | + | ++ |
| Drilled | 90+ | Mar. | {Cl = 438 Solids 4000} | .. | 720 | + | + | + | + | ++ | ++ |
| Drilled | 50+ | Mar. | Bad | 200 | 5,000 | + | — | + | + | + | ++ |
| Driven | 85 | Apr. | Good | 12 | 100 | + | + | + | + | + | — |
| Driven | 50+ | May | Poor | 95 | 3,000 | + | — | — | — | ? | ++ |
| Dug | 22 | May | Bad | 290 | 590 | + | — | — | ? | Trace | + |
| Drilled | 25 | May | Bad | 55 | 700 | + | — | — | ? | ++ | ++ |
| Dug | 16 | June | Poor | 650 | 1,500 | + | — | — | ? | ++ | ++ |
| Dug | 30 | June | Poor | 8 | 2,000 | + | — | + | + | — | Trace |
| Dug | 30 | June | Poor | 25 | 2,000 | + | + | + | + | + | ++ |
| Dug | .. | June | Suspicious | 3 | 1,000 | — | — | — | — | — | Trace |
| Artesian | 286+ | July | Good | .. | 35 | — | — | — | — | — | — |
| Dug | 40? | July | Good | 10 | 250 | + | — | — | ? | + | ++ |
| Drilled | .. | July | Suspicious | 70 | 145,000 | + | — | — | ? | ? | ++ |
| Dug | 17 | July | Suspicious | 2,000 | 50,000 | + | + | + | + | + | ++ |
| Dug | 20 | July | Poor | 3,000 | 18,000 | + | + | + | + | — | + |
| Driven | 16 | July | Good | 9 | 35 | + | — | — | — | — | + |
| Drilled | 165 | July | Bad | 2 | 170,000 | — | — | — | — | — | — |

TABLE IV.—WELL WATERS (Continued).

| Kind of well. | Depth in test. | Month of year. | Quality from chem. anal. | Colonies per cc. on | | Gas producers. | Color group present in | | | Indol production. | Hydrogen sulfide production. |
|---------------|----------------|----------------|--------------------------|---------------------|--------------|----------------|------------------------|-------|--------|-------------------|------------------------------|
| | | | | Agar 38°. | Celatin 20°. | | 1 cc. | 5 cc. | 10 cc. | | |
| Driven | 75 | Aug. | Good | 750 | 2,000 | + | — | — | — | — | — |
| Artesian | 428 | Aug. | Good | 250 | 500 | + | — | — | — | — | — |
| Dug | 17 | Aug. | Suspicious | 2,500 | 15,000 | + | + | + | + | + | + |
| Drilled | 165 | Aug. | Bad | 1,800 | 18,500 | — | — | — | — | — | Trace |
| Drilled | 115 | Aug. | Good | 200 | 75,000 | + | — | — | ? | ? | + |
| Drilled | 25 | Aug. | Bad | 60,000 | 50,000 | — | — | — | — | Trace | + |
| Driven | 41 | Sept. | Good | .. | 330 | + | — | ? | ? | + | + |
| Dug | .. | Sept. | Poor | 4 | 70 | — | — | — | — | ? | Trace |
| Dug | 16 | Sept. | Good | 25 | 750 | + | — | — | — | — | — |
| Dug | 20 | Sept. | Poor | 1,100 | 3,800 | + | + | + | + | + | + |
| Driven | 50 | Oct. | Suspicious | 60 | 130 | + | — | + | + | — | + |
| Driven | 46 | Oct. | Poor | 5 | 10 | + | — | — | ? | + | + |
| Driven | 80+ | Oct. | Good | 0 | 6 | + | — | — | — | — | — |
| Dug | .. | Oct. | Poor | 35 | 300 | + | — | — | — | — | — |
| Dug | .. | Oct. | Good | 3,900 | 39,000 | + | — | — | ? | + | + |
| Dug | .. | Oct. | Poor | 5 | 100 | + | — | ? | + | + | + |
| Artesian | 303 | Oct. | Good | 15 | 3 | — | — | — | — | — | — |
| Artesian | 286 | Oct. | Good | 2 | 3 | — | — | — | — | — | — |
| Artesian | 280 | Oct. | Good | 4 | 3 | — | — | — | — | — | — |
| Artesian | 276 | Oct. | Good | 1 | 2 | — | — | — | — | — | — |
| Dug | 12 | Oct. | Good | 100 | 1,400 | + | — | — | — | + | + |
| Dug | 20± | Oct. | Bad | 30 | 120 | — | — | — | — | + | + |
| Dug | 15 | Oct. | Bad | 60 | 550 | + | ? | + | + | + | + |
| Driven | .. | Oct. | Bad | 30 | 130 | + | + | + | + | + | + |
| Dug | .. | Dec. | Suspicious | 500 | 1,500 | + | — | ? | + | + | + |
| Dug | 40 | Dec. | Suspicious | 20 | 500 | + | — | — | ? | + | + |

In routine testing, therefore, it is advantageous to use flasks with wide neck tubes of large diameter in order that a considerable surface shall be exposed to the air.

In the accompanying tables are given the results obtained with the tests for hydrogen sulfide production upon a number of different water samples. Although the data have been greatly abridged it is hoped that sufficient information has been given to enable the reader to properly grade the water samples. Since most natural waters usually exhibit a very marked seasonal change in their bacterial flora, the samples have been tabulated by months.

TABLE V.—MISCELLANEOUS WATERS.

| Source of sample. Water. | Month of year. | Quality from chem. anal. | Colonies per cc. on | | Gas production. | Colon group present in | | | Indol production. | Hydrogen sulphide production. |
|-----------------------------|----------------|--------------------------|---------------------|--------------|-----------------|------------------------|-------|--------|-------------------|-------------------------------|
| | | | Agar 38°. | Gelatin 20°. | | 1 cc. | 5 cc. | 10 cc. | | |
| Stored, ground | Jan. | Good | 0 | 50 | — | — | — | — | + | — |
| Ice | Jan. | Poor | 2 | 3,000 | — | — | — | — | — | Trace |
| Ice | Feb. | Good | 1 | 13 | — | — | — | — | — | Trace |
| Ice | Feb. | Good | 2 | 10 | — | — | — | — | — | — |
| Ice | Feb. | Poor | 10 | 110 | + | — | — | + | + | +++ |
| Ice | Mar. | Poor | 25 | 900 | — | — | — | — | — | — |
| Tank wagon | July | Good | 30 | 450 | — | — | — | — | — | — |
| Tank wagon | Aug. | Good | 70 | 1,400 | + | + | + | + | + | ++ |
| Cistern, rain | Oct. | Poor | 3,300 | 45,000 | + | — | ? | ? | ++ | +++ |
| "Sterilized"* | Oct. | Poor | 10,000 | 15,000 | + | + | + | + | Trace | Trace? |
| "Sterilized" | Oct. | Good | 325 | 1,200 | — | — | — | — | Trace | + |
| Tank wagon | Nov. | Good | 350 | 10,000 | + | + | + | + | Trace | +++ |
| Bottled spring | Nov. | Good | 750 | 1,500 | + | ? | + | + | — | — |
| "Sterilized" | Nov. | Poor | 1 | 270 | — | — | — | — | — | Trace |
| Stored, ground | Dec. | Good | 0 | 10 | — | — | — | — | — | — |
| Stored, ground | Dec. | Bad | 1,000 | 6,300 | + | + | + | + | + | ++ |

*From small plant using a patented "water sterilizer."

Summary of Results Obtained.

1. Irrespective of the inorganic salts present and of the acidity of the medium, a concentration of between 3 and 4% peptone in the final inoculated and incubated medium appears to be best for the most rapid and energetic production of hydrogen sulfide.

2. The addition of beef broth to simple peptone media slightly increases its sensitiveness, but not in proportion to the increased trouble and labor involved.

3. If sodium chloride is used, the quantity added must not be over 1.5%. Cultures to which this salt was added showed greater hydrogen sulfide production than those which contained none.

4. In 3% peptone media, the presence of from 0.5% to 1% of potassium chloride had a decidedly beneficial influence and led to quicker, better and far more uniform results than any other inorganic salt tried.

5. Positive results of hydrogen sulfide formation may be obtained in eighteen hours.

6. No hydrogen sulfide formation is obtainable in as long a period as seventy-two hours from natural waters which are truly "clean," while much is formed in from twelve to twenty-four hours with contaminated waters.

7. The feces of domestic animals contain bacteria which are capable of producing hydrogen sulfide from a simple peptone medium in as large amounts as is the case of the bacteria from human feces.

8. The large amounts of hydrogen sulfide *rapidly* produced by organisms of sewage appears to be not due primarily to members of the *B. coli* group.

9. This group of hydrogen sulfide producing bacteria do not actively ferment carbohydrates. Hence testing for their presence is a valuable aid supplementing tests for gas producers and is of especial value in polluted waters in which the *B. coli* group is absent.

10. Some evidence has been obtained which apparently indicates that hydrogen sulfide is more rapidly produced in waters containing a mixed bacterial flora than by the isolated pure cultures alone.

LABORATORY OF SANITARY CHEMISTRY,
CORNELL UNIVERSITY.

[CONTRIBUTION FROM THE COLLEGE OF AGRICULTURE, THE UNIVERSITY OF MINNESOTA.]
**ON THE ORIGIN OF THE HUMIN FORMED BY THE ACID
'HYDROLYSIS OF PROTEINS.**

BY ROSS AIKEN GORTNER AND MORRIS J. BLISH.

Received April 10, 1915.

Introduction.

It is well known that, when proteins are subjected to hydrolysis by boiling acids, a blackening of the solution occurs, and that, when the boiling is continued for some time, black insoluble particles separate from solution. These compounds may be purified to a greater or a less degree by solution in alkali and reprecipitation by the addition of acid. They are, however, insoluble in all of the usual organic solvents and have never been obtained in crystalline form.

A very considerable amount of work has been done on these humins or "melanoidins" as Schmiedeberg¹ calls them. Schmiedeberg found that indol and skatol were formed in an alkali fusion and Samuley² by reduction obtained evidences of pyridine formation. Inasmuch as humin was not formed from proteins when the hydrolysis was carried out in the presence of stannous chloride, Samuley concludes that the formation of this dark-colored product is due to an oxidative process.

¹ *Arch. Exper. Path. u. Pharm.*, 39, 1-84 (1897).

² *Beitr. chem. Physiol. u. Path.*, 2, 355-88 (1902).

The question as to the nature of the mother substance from which these humins are formed is of the greatest importance. In a study of the nitrogen partition of proteins it often happens that several per cent. of the total nitrogen must be recorded as "humin nitrogen."¹ All of the other fractions obtained in the nitrogen partition can be correlated with known structures in the protein molecule, but the humin nitrogen has no known meaning other than that it varies in the different proteins.

The questions therefore remain: *Is the humin nitrogen derived from some known product of protein hydrolysis, or is it formed from some unknown constituent?* If it is formed from some known amino acid, can the reaction not be made quantitative and thus form a basis for the estimation of this amino acid?

In an attempt to answer the above questions we have performed a few experiments. We believe that we have answered the first question, and that we have secured some evidence which may help to answer the second question.

Osborne and Jones,² in a study of the hydrolysis products of proteins, state:

"There can be no doubt that this substance (humin) is a mixture of the secondary decomposition products formed from different constituents of the protein by the action of acids, for some of these, such as tryptophane, histidine, and carbohydrate, are known to yield colored products under such conditions. That the melanin originates chiefly from these substances is indicated by the fact that zein, which gives no reaction for tryptophane or carbohydrate and yields only a small amount of histidine, gives rise to the merest trace of humin when subjected to prolonged hydrolysis with acids."

Van Slyke³ later took up one phase of this problem in so far as tryptophane was concerned. He boiled 0.9 g. of tryptophane for 12 hours with 100 cc. of 20% hydrochloric acid and concentrated the solution *in vacuo*. He states:

"The solution was clear, free from insoluble matter, and but very slightly colored. . . . *Tryptophane is responsible for none of the nitrogen estimated as ammonia, arginine, or melanin.*"

In view of Osborne's statement that zein yielded almost no humin and that tryptophane, was not present it seemed possible that Van Slyke might be in error as to his conclusions. It will be noted that he boiled the tryptophane alone, and not in the presence of other products of protein hydrolysis. It therefore seemed advisable to mix zein with definite amounts of tryptophane and to submit the mixture to acid hydrolysis and then secure the nitrogen partition on the hydrolyzed mixture.

¹ Owing to the similarity of this humin, both in color and solubility, to the naturally occurring melanins it is often referred to as "melanin" and its nitrogen as "melanin nitrogen." One of us (Gortner, 1912, *Science*, n. s. 36, 52-3) has already pointed out that other criteria of relationship should be secured before such a confusing terminology is adopted.

² *Am. J. Physiol.*, 26, 305-28 (1910).

³ *J. Biol. Chem.*, 10, 15-55 (1911).

Experimental.

The purity of the material was the first consideration. The zein employed in the following experiments was from a sample kindly given us by Professor Osborne. A Kjeldahl determination of nitrogen gave only 15.25%. This figure is lower than that given by Osborne,¹ 16.13%, but it is probable that our sample contained moisture, inasmuch as we did not deem it advisable to dry it with the aid of heat.

The tryptophane was prepared by the tryptic digestion of casein and subsequent separation by the method of Hopkins and Cole.² The product was repeatedly treated with bone-black and recrystallized from dilute alcohol. It was obtained in the form of almost colorless nacreous plates.

Nitrogen found, 14.06%; calc., 13.72%. Amino nitrogen (by van Slyke's apparatus): found, 6.81%; calc., 6.86%.

Histidine-di-hydrochloride was prepared from cattle blood.³

Amino nitrogen found, 6.07%; calc., 6.14%.

The dextrose was from a sample prepared by the U. S. Bureau of Standards and contained no nitrogen.

The method of analysis was as follows: to the protein + the added substances 50 cc. of hydrochloric acid, sp. gr. 1.115, was added, and the mixture was boiled under a reflux condenser for 48 hours. The acid was distilled off under diminished pressure and ammonia nitrogen determined according to Van Slyke⁴ by distilling with calcium hydroxide at 40-45° under a pressure of less than 30 mm.

The residue remaining in the distilling flask was filtered and the precipitate containing the humin washed with hot water to the absence of chlorides. A Kjeldahl nitrogen determination on the filter and its contents gave the humin nitrogen.

The filtrate from the humin was concentrated to about 100 cc., 10 cc. of concentrated hydrochloric acid and 7.5 g. of phosphotungstic acid were added and the mixture heated for a few minutes on a water bath and then allowed to stand in a cool place for 48 hours. The phosphotungstates of the bases were then filtered off and washed as described by Van Slyke.

The entire precipitate was used for a Kjeldahl nitrogen determination.

The results of the analyses may be found in the accompanying table.

When zein was hydrolyzed alone the solution did not become intensely black but when tryptophane had been added the black color developed sooner and was much more intense. Besides the black color there was a distinct reddish color in the hydrolysate from the zein + tryptophane, the filtrate from the humin, as well as from the phosphotungstate precipitate, being likewise darker in the case of added tryptophane.

In the ammonia determinations when tryptophane had been added in large amount there was an intense frothing toward the end of the distillation, after the alcohol had largely distilled off. In no other material have we obtained such a result.

¹ "The Vegetable Proteins," 1912, Longmans, Green & Co., N. Y.

² As described in "Handb. d. Biochem. Arbeitsmethoden," Vol. II, pp. 487-8.

³ As described in "Handb. d. Biochem. Arbeitsmethoden," Vol. II, p. 505.

⁴ *Loc. cit.*

TABLE I.—SHOWING THE WEIGHTS OF NITROGEN AND THE PERCENTAGE OF TOTAL NITROGEN OBTAINED IN THE VARIOUS FRACTIONS FROM THE DIFFERENT EXPERIMENTS.

| Material hydrolyzed. | Ammونيا N. | Humus N. | Basic N. | Nonbasic N. | Total N found. | Total N calc. |
|---|------------|-----------|------------|-------------------|----------------|---------------|
| 1 g. zein ¹ | 0.03164 g. | 0.0007 g. | 0.00489 g. | 0.1184 g. | 0.1546 g. | 0.1525 g. |
| *..... | 20.75% | 0.46% | 3.21% | 77.66% | 102.08% | |
| 1 g. zein + 0.25 g. tryptophane..... | 0.0290 g. | 0.0070 g. | 0.01603 g. | 0.1348 g. (calc.) | | 0.1868 g. |
| | 15.52% | 3.75% | 8.58% | 72.15% (calc.) | | |
| 1 g. zein + 0.125 g. tryptophane..... | 0.0316 g. | 0.0077 g. | 0.0056 g. | 0.1241 g. | 0.1690 g. | 0.1696 g. |
| | 18.63% | 4.54% | 3.30% | 73.14% | 99.61% | |
| 1 g. zein + 0.2312 g. histidine-dihydrochloride..... | 0.0316 g. | 0.0010 g. | 0.0497 g. | 0.1128 g. (calc.) | | 0.1951 g. |
| | 16.20% | 0.51% | 25.48% | 57.81% (calc.) | | |
| 0.5 g. zein + 0.5 g. dextrose..... | 0.0154 g. | 0.0014 g. | | | | 0.0762 g. |
| | 20.20% | 1.84% | | | | |
| 0.5 g. zein + 0.5 g. dextrose + 0.125 g. tryptophane..... | 0.0158 g. | 0.0154 g. | | | | 0.0933 g. |
| | 16.93% | 16.50% | | | | |
| 0.125 g. tryptophane + 0.5 g. dextrose.... | None | 0.0148 g. | | | | 0.0171 g. |
| | | 86.56% | | | | |
| Approx. 0.1 g. tryptophane..... | None | None | | | | 0.0137 g. |
| 1 g. gliadin..... | 0.0451 g. | 0.0010 g. | 0.0071 g. | 0.1168 g. (calc.) | | 0.1700 g. |
| | 26.54% | 0.59% | 4.17% | 68.73% (calc.) | | |
| 1 g. gliadin + 0.25 g. dextrose..... | 0.0454 g. | 0.0016 g. | 0.0068 g. | 0.1162 g. (calc.) | | 0.1700 g. |
| | 26.71% | 0.94% | 4.00% | 68.37% (calc.) | | |
| 1 g. gliadin + 2 g. dextrose..... | 0.0450 g. | 0.0039 g. | 0.0063 g. | 0.1148 g. (calc.) | | 0.1700 g. |
| | 26.47% | 2.30% | 3.70% | 67.53% (calc.) | | |

¹ Osborne gives the nitrogen partition of zein as ammonia N 18.4%, humin N 0.99%, basic N 3.0%, nonbasic N 77.5%. The amount of humin nitrogen varied in Osborne's determinations from 0.31% to 1.48% in different determinations. See Osborne and Harris, *THIS JOURNAL*, 25, 323 (1903). Our higher percentage of ammonia nitrogen is probably due to a longer hydrolysis.

Discussion.

It will be seen from the table that Van Slyke's conclusion that tryptophane nitrogen is not transformed into humin nitrogen holds true only when tryptophane is boiled alone. When, however, tryptophane is added to a protein a very considerable portion of the tryptophane nitrogen passes into the humin fraction (approx. 0.0070 g. when tryptophane is added to 1 g. of zein). The remainder of the tryptophane nitrogen is distributed between the bases and the filtrate from the bases. In no case does added tryptophane cause an increase in the ammonia nitrogen.

From Experiments 2 and 3 it will be seen that the formation of humin from tryptophane had reached a maximum when 0.125 g. of tryptophane had been added, since no additional humin nitrogen was obtained when 0.25 g. of the amino acid was added. This observation shows, as does the fact that no humin is formed from the pure tryptophane, that the reaction involves not only tryptophane but also some other product of hydrolysis. We therefore boiled dextrose + tryptophane, zein + dextrose and zein + dextrose + tryptophane and found that when tryptophane was heated in the presence of a carbohydrate practically 90% of the tryptophane nitrogen remained in the humin fraction. It seems very possible that with a slightly longer hydrolysis, or with the altering of some of the conditions of hydrolysis that the reaction might have been made quantitative. It is, however, nearly enough quantitative for our present purpose, and we did not have sufficient material to work out the ideal conditions of the reaction.

It is well known that when carbohydrates are boiled with mineral acids a small amount of furfural is formed and it seems highly probable that the reaction involved in humin formation is a condensation of tryptophane with an aldehyde. Miss Homer¹ has prepared condensation products of tryptophane with various aldehydes and states:

"Indol derivatives by virtue of the —NH group in the nucleus will react with formaldehyde and trioxymethylene in the presence of a condensing agent to form substances of intense color and marked insolubility in ordinary solvents other than concentrated mineral acids."

When, however, the condensation takes place on the aliphatic —NH_2 group, colorless, crystalline compounds are formed.

From our experiments with zein + dextrose it appears certain that the humin nitrogen is not a result of an absorption phenomenon. The hydrolysate in this instance was jet-black and full of suspended flecks of solid humin formed by the decomposition of the carbohydrate, while the humin nitrogen was but slightly in excess of the experimental error, considering the relatively large amount of humin and lime to be washed free from nitrogen.

The fact that the hydrolysis of zein does give rise to some humin, and

¹ *Biochem. J.*, 7, 101-115 (1913).

that there is a slight increase in the humin nitrogen due to the addition of glucose may, however, be due to the presence of tryptophane in the zein molecule in such small quantity that it is difficult to detect with the color tests. For a long time gliadin was supposed to contain no lysine, but Van Slyke¹ found it to be present in this protein, and his findings were later confirmed by Osborne and Leavenworth.²

Osborne and Harris³ state:

"Whether any of the above proteins wholly lack tryptophane could not be determined, as we were able to get a very slight reaction with a relatively large quantity of zein by cautiously adding the sulfuric acid up to one-half the volume of the glyoxylic acid. The color thus produced was, at the most, very slight and transitory."

Mann⁴ in a discussion of the humin formed from carbohydrates states:

"If in addition to the carbohydrate, ammonia or other nitrogenous substances are in solution, then the humins combine with the ammonia and thereby become nitrogenous."

We do not believe that this reaction, if it takes place at all, can be any great factor in the formation of the humin nitrogen of protein hydrolysis, for our analyses show a variation in the amount of ammonia nitrogen which is certainly not much greater than the experimental error. Thus we have 0.0154 g. of ammonia *N* from 0.5 g. of zein hydrolyzed in the presence of 0.5 g. of dextrose, and 0.0316 g. of ammonia *N* from 1 g. zein when hydrolyzed alone, a difference of only 0.0008 gram *N* calculated on a 1 g. basis. Again there is a loss of only 0.0001 g. ammonia *N* when 1 g. of gliadin was hydrolyzed in the presence of 2 g. of dextrose. In this instance there is an increase in the humin nitrogen and it is of interest to note that this increase comes from the bases and the filtrate from the bases in the ratio of approximately 4:6, almost the identical ratio (38.7:61.3) which Van Slyke⁵ finds for the distribution of tryptophane between the bases and the filtrate from the bases.

Experiment 4 indicates that histidine has no part in the formation of humin nitrogen, since there was no increase in color over that produced when the zein was hydrolyzed alone, and there was no significant increase in the humin nitrogen, the histidine nitrogen being quantitatively recovered in the bases.

We believe, therefore, that we have shown that, in a large measure at least, the humin nitrogen represents a portion of the tryptophane nitrogen, and that if sufficient carbohydrate be present the humin nitrogen can be regarded as an almost quantitative determination of the tryptophane nitrogen. What reaction takes place when no carbohydrate is present

¹ *J. Biol. Chem.*, **10**, 15-35 (1911).

² *Ibid.*, **14**, 481-7 (1913).

³ *THIS JOURNAL*, **25**, 853-5 (1903).

⁴ "Chemistry of the Proteids," p. 88, 1906, MacMillan & Co., N. Y.

⁵ *Loc. cit.*

and humin nitrogen is formed, as in Experiments 2 and 3, we are unable to state. Various possibilities present themselves, such as the oxidation of tryptophane itself to indol aldehyde, which would in turn unite with more tryptophane to form a deeply colored, insoluble compound,¹ or possibly traces of some other amino acid may be oxidized to the corresponding aldehyde. Isham and Vail² have recently shown that ether is readily oxidized to aldehyde by atmospheric oxygen at 110°. A contamination of the protein with a small amount of ether, or of the aldehyde formed from the ether during extraction, would account for this humin formation, if tryptophane were present. We regret that lack of material prevented our trying further experiments in this direction.

Summary.

1. We have shown that in all probability the humin nitrogen of protein hydrolysis has its origin in the tryptophane nucleus.

2. When tryptophane is boiled with mineral acids in pure solution no humin is formed, but when tryptophane is added to a protein, or when carbohydrates are present, an abundance of humin is formed. This humin contains nitrogen which can belong to no amino acid other than tryptophane.

3. The reaction involved in humin formation is probably the condensation of an aldehyde with the —NH group of the tryptophane nucleus.

4. When an abundance of carbohydrate is present nearly 90% of the tryptophane nitrogen remains in the humin nitrogen fraction.

It is suggested that this property be utilized to determine the approximate quantity of tryptophane in proteins.

5. The addition of histidine causes no increase of humin nitrogen, the histidine being quantitatively recovered in the bases. Histidine, therefore, can be eliminated as a factor in the formation of humin nitrogen.

6. Adsorption of ammonia by non-nitrogenous humins formed from carbohydrates is not an important factor in the formation of humin nitrogen.

7. These findings allow us to assign a distinct value to humin nitrogen determinations.

ST. PAUL, MINN.

NOTE.

On Rapid Organic Combustions.—The use of cerium dioxide as contact substance for rapid organic combustions, in place of the more expensive platinum of Dennstedt, has recently been recommended.³ In trying out the method in this laboratory, it has been found that it is not entirely

¹ Homer, *Biochem. J.*, 7, 116 (1913).

² *THIS JOURNAL*, 37, 902 (1915).

³ Julius Bekk, *Ber.*, 46, 2574 (1913).

satisfactory in the hands of beginners. The reasons for this are two: first, part of the substance is carried through the tube unburned if the stream of oxygen is even a little too slow or, on the other hand, so rapid that the vapor of the substance mixed with oxygen is carried too quickly past the catalyst; second, after the asbestos impregnated with cerium dioxide has been used several times, it crumbles to a fine powder and a slight amount of this may be carried into the absorption apparatus if the stream of oxygen is very rapid.

These difficulties can be overcome by the following modification of the method: Instead of the large quantity of asbestos, impregnated with cerium dioxide, recommended by Bekk, a layer of cerium dioxide asbestos only 3 cm. long is placed in the center of a combustion tube of the usual length. Following this is a 20 cm. layer of cupric oxide in wire form, held in place by a cupric oxide gauze plug. The cupric oxide furnishes oxygen for the burning substance in case the supply of gaseous oxygen is insufficient, or if the vapor of the substance has been carried too fast over the catalyst, and prevents the dust of the cerium dioxide from being carried forward in the tube.

In the back end of the tube is the usual 10 cm. cupric oxide gauze spiral. This serves to break the stream of oxygen and does away with the necessity for the "double oxygen" apparatus of Dennstedt and the glass tube surrounding the boat recommended by Dennstedt and by Bekk.

The absorption apparatus described by Dennstedt in an early paper¹ has been found perfectly satisfactory. It consists of the usual calcium chloride U-tube and two 12 cm. U-tubes with ground glass stoppers.² The one next the calcium chloride tube is filled with soda-lime, the other contains solid potash with a 2.5 cm. upper layer of fused calcium chloride in each arm. The soda-lime tube can be used for two combustions; the potash tube almost indefinitely.

The procedure differs from that of the usual method in the following points: The combustion boat should be placed not more than 2 cm. from the cerium dioxide asbestos. This is important, as explosive mixtures of gases form if there is any considerable space in which the vapor of the substance and oxygen can mix before they come in contact with the catalyst. As soon as the front end of the tube is hot and the boat in place, a rapid stream of oxygen is turned on and the forward burners are lighted to within about 8 cm. of the boat. If the substance to be burned is very volatile, the stream of oxygen should be less rapid and the cerium dioxide asbestos more cautiously heated by first placing above it hot tiles from the forward

¹ "Entwicklung der Organischen Elementaranalyse." Sammlung chemischer und chemisch-technischer Vorträge, Ahrens, Stuttgart, 1899, p. 105.

² Leakage at the stoppers can be prevented by using the rubber lubricant recommended by Richards (Carnegie Institution of Washington, Publication No. 56, 16 (1906)).

end of the tube. As the vapor of the substance and oxygen come in contact with the hot cerium dioxide, the latter glows brightly. The soda-lime tube becomes very hot from the absorption of carbon dioxide. When the glowing has ceased and the *soda-lime tube cools*, the combustion is ended.

The following results have been obtained:

| | | | | | |
|----------------------------------|-------------------|---------|---|-------------------|---------|
| Succinic Acid, 0.2028 g. | | | Salicylic Acid, 0.1975 g. | | |
| | Time, 17 minutes. | | | Time, 11 minutes. | |
| Calc. for $C_4H_6O_4$: | C, 40.66 | H, 5.08 | Calc. for $C_7H_6O_3$: | C, 60.85 | H, 4.34 |
| Found: | C, 40.57 | H, 5.12 | Found: | C, 60.66 | H, 4.37 |
| Benzoic Acid, 0.1749 g. | | | Naphthalene, 0.1888 g. | | |
| | Time, 9 minutes. | | | Time, 13 minutes. | |
| Calc. for $C_7H_6O_2$: | C, 68.85 | H, 4.91 | Calc. for $C_{10}H_8$: | C, 93.75 | H, 6.25 |
| Found: | C, 68.67 | H, 5.10 | Found: | C, 93.61 | H, 6.31 |
| Sugar, 0.2080 g. | | | Methyl Dibenzylidene Phenyl Glutarate, 0.1585 g. | | |
| | Time, 18 minutes. | | | Time, 14 minutes. | |
| Calc. for $C_{12}H_{22}O_{11}$: | C, 42.10 | H, 6.43 | Calc. for $C_{27}H_{28}O_4$: | C, 78.64 | H, 5.82 |
| Found: | C, 42.17 | H, 6.44 | Found: | C, 78.80 | H, 6.05 |

Aside from the great saving of time, the method is satisfactory for beginners, in that it is free from some of the usual sources of difficulty; water does not draw back in the tube nor collect around the forward stopper because of the rapid stream of oxygen, and there is no danger of burning the stoppers, since it is not necessary to heat the tube near the ends.

A disadvantage is that the method cannot be used for the simultaneous determination of carbon, hydrogen and halogens as can the Bekk method where no cupric oxide is used. It is available however, for the analysis of compounds containing nitrogen if a longer empty space is left at the forward end of the tube for the boats of lead peroxide¹ and care is taken to keep that end of the tube fairly cool. The combustion should be run a little less rapidly than with carbon and hydrogen alone.

The following results have been obtained:

| | | | | | |
|--|-------------------|---------|------------------------|-------------------|---------|
| Acetamid, 0.1707 g. | | | Acetanilid, 0.1788 g. | | |
| | Time, 28 minutes. | | | Time, 24 minutes. | |
| Calc. for C_8H_9NO : | C, 40.67 | H, 8.47 | Calc. for C_8H_9NO : | C, 71.11 | H, 6.66 |
| Found: | C, 40.91 | H, 8.42 | Found: | C, 71.01 | H, 6.70 |
| Propyl Cyancinnamylideneacetate, 0.1591 g. | | | | | |
| | Time, 25 minutes. | | | | |
| Calc. for $C_{18}H_{19}NO_3$: | C, 74.68 | H, 6.22 | | | |
| Found: | C, 74.46 | H, 6.16 | | | |

MARIE REIMER.

CHEMICAL LABORATORY, BARNARD COLLEGE,
March, 1915.

¹ Cf. Dennstedt, "Anleitung zur vereinfachten Elementaranalyse," III Aufl. Hamburg, 1910, p. 66.

NEW BOOKS.

- (a) **The Numerical Data of Spectroscopy.** By L. BRÜNINGHAUS, with a preface by H. Deslandres. Published with the assistance of the Ministère de l'Instruction publique. Pp. 74. (b) **The Numerical Data of Electricity, Magnetism, and Electro-chemistry.** By P. DUBOIS, W. C. McC. LEWIS and A. MAHLKE, with a preface by M. LeBlanc. Published under the auspices and with the assistance of the Ministère du Commerce, de l'Industrie et des Postes et Télégraphes, the Comité des Forges de France, the Société des Ingénieurs civils, and the Société Internationale des Électriciens. Pp. 79. (c) **The Numerical Data of Radioactivity.** By J. SAPHORES and F. BOURION. Published with the assistance of the Institut de Radioactivité de l'Université de Paris. Pp. 9. (d) **The Numerical Data of Crystallography and Mineralogy.** By M. L. J. SPENCER, with the preface by A. Lacroix. Published under the auspices and with the assistance of the Deutsche mineralogische Gesellschaft, the New York Academy of Sciences, the Société française de Minéralogie, the Société impériale russe de Minéralogie, The Mineralogical Society, and the Wiener Mineralogische Gesellschaft. Pp. 19. (e) **The Numerical Data of Biology.** By EMIL F. TERROINE, with a preface by E. Roux and an introduction by Dr. Delezenne. Published under the auspices of the Institut Pasteur de Paris. Pp. 17. (f) **The Numerical Data of Engineering and Metallurgy.** By S. L. ARCHBUTT, G. FIECK, W. HINRICHSSEN, E. NUSBAUMER and A. PORTEVIN, with a preface by A. Mesnager. Published under the auspices and with the assistance of the Ministère des Travaux Publiques, the Comité des Forges de France, the Groupe Franco-Belge de l'Association Internationale pour l'Essai des Matériaux, the Iron and Steel Institute, the Société des Ingénieurs Civils, and the Société Industrielle de l'Est. Pp. 74.

This series of six sets of tables is made up of data extracted from Volume 3 of the **Annual Tables of Physical Constants and Numerical Data** and is issued in this form in order that selected classes of data may be made available at a lower price and in a more convenient form. The books are issued by the University of Chicago press and are listed at the following prices: *a*, *b*, and *f*, 10 francs each; *c*, 2 fr. 50; *d* and *e*, 4 fr. each.

E. W. WASHBURN.

Handbuch der Mineralchemie. DOBLER, *et al.* Bd. II. No. 7 (Bogen 11-20). Theodor Steinkopff, Dresden and Leipzig. Price, M. 6.50.

In scanning these pages the reader is struck by the great amount of space devoted to the *formulae* of mineral substances. The remarkable fruitfulness of this form of study in the organic field has inevitably affected the development of mineral chemistry. To disparage work of this character would serve only to define the interests of the critic, but at least we may say that the results have not been at all commensurate with those in organic chemistry and that speculation so far from the facts as much of this is cannot be expected to advance science materially. It seems to the reviewer that much of the matter on this subject and mineralchemie might be condensed to advantage.

There are several subjects in this issue of Mineralchemie of more than average interest, notably the nephelinite group of mineral and the ultramarines.

E. T. ALLEN.

been shown in every line, and particularly in the places where the literature is confused and most authors blunder more or less seriously. Part II (67 pp.) deals with the nonvalent group of elements. It gives a condensed, but lucid and very complete summary of all that is known about the inert gases. Judging from the initial volume, the whole book will be an indispensable work of reference that should be on the desk of every chemist.

ALEXANDER SMITH.

I. A. R. I. 75.

IMPERIAL AGRICULTURAL RESEARCH
INSTITUTE LIBRARY
NEW DELHI.

[illegible]